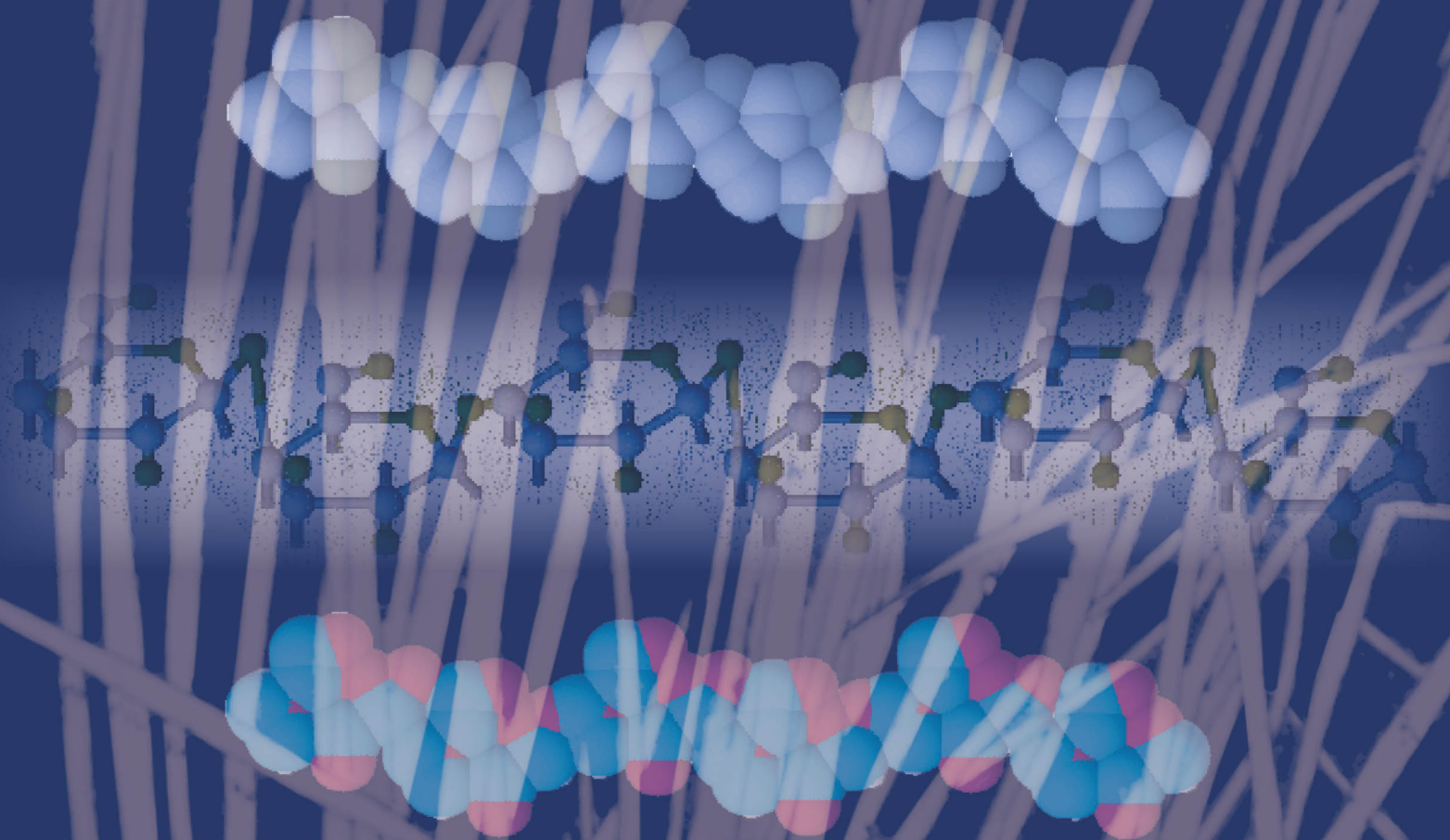


INTRODUCTION TO
**Polymer
Chemistry**
FOURTH EDITION



Charles E. Carraher Jr.

 **CRC Press**
Taylor & Francis Group

Introduction to Polymer Chemistry

Fourth Edition



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Introduction to Polymer Chemistry

Fourth Edition

Charles E. Carraher, Jr.



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Preface

Polymers are all about us and are responsible for life itself, for communication (both natural and synthetic), for our nutrition, clothing, recording history, buildings and highways, and numerous other applications. In fact it is difficult to imagine society without synthetic polymers and life without natural polymers. Part of being an educated and responsible citizen involves knowing the correct questions to ask and knowing (possible) correct answers. In our ever-increasingly technological world, science plays a crucial role in providing solutions to critical problems of food, clean and abundant water, energy, and air; environment; and health. This text provides both the information and insights that allow a better understanding of these large molecules that are all about us. This text includes the elements required by the American Chemical Society Committee on Professional Training in their current guidelines with respect to the requirement that polymers be included in the undergraduate curriculum.

There is an appropriate and necessary move toward green materials and green chemistry. This trend is captured in the present book, within the appropriate sections and with the addition of a separate section on green materials. There also exists a greater awareness of health concerns within our society, and this awareness is mirrored in this text.

Most polymer texts are aimed at either graduate students or are hybrids aimed at both the undergraduate and, mostly, graduate students. This text is aimed mainly at undergraduate students and is suitable for students pursuing fields outside of chemistry. Information gained from the basic core science courses is applied for understanding giant molecules. This information includes factual, theoretical, and

practical concepts present in polymer science. This text is useful to those that simply want to be well educated, as well as those wanting to pursue medicine, engineering, physics, chemistry, environmental sciences, biomedical sciences, law, and business.

This text is inclusive in the treatment of polymers including natural and synthetic giant molecules; inorganic and organic polymers; biomacromolecules; and elastomers, adhesives, coatings, fibers, plastics, blends, caulks, composites, and ceramics. The basic principles that apply to one polymer grouping apply to all of the other groupings when applied with some simple fundamentals. These fundamentals are integrated into the fabric of this text.

We remember the saying “we should be students of history so we do not repeat the same mistakes”; we should also be students of history so that we might repeat the successes. Thus, a strong bond is forged between science, history, and the crucible that is today’s society. Brief case studies are woven within the fabric of the text as historical accounts illustrating the purposes in back of change as well as the societal and scientific context within which these changes occurred.

This edition is in full color. The use of color is intended to aid in describing basic concepts. It also contains many photographs that allow the reader to grasp the importance of polymers in our everyday lives.

About the cover: Cellulose unit structures are superimposed onto cattails presented in a mixed media of pen and ink and water color drawn by the author.



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Charles E. Carraher, Jr. is professor of chemistry and biochemistry, Florida Atlantic University, Boca Raton. Recognized as outstanding chemist in the Southeast United States (1992) by the American Chemical Society and the recipient of a Distinguished Service Award for his efforts in science education (1995) from the ACS's Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering, he is a fellow of the American Institutes of Chemists (1975), Polymeric Materials (2006), Polymer Chemistry (2010), and the American Chemical Society (2010). Currently, he serves as cochair of the ACS's Joint Polymer Education Committee and on the Board of the Intersocietal Polymer Education Committee and has been a member of the ACS's Committee on Professional Training (CPT). He is associate editor of the *Journal of Polymeric*

Materials and on the board of the *Journal of Inorganic and Organometallic Polymers and Materials* and the *International Journal of Polymeric Materials and Polymeric Biomaterials*. The author or coauthor of over 75 books and over 1000 articles, he has chaired/cochaired numerous national and international symposia. His research has led to the synthesis of over 75 new families of polymers. In 1984, he received the Outstanding Scientist and Engineering Award from the Engineers and Scientists Affiliate Societies Council for his work in science education and research, and in 1992 the Saltarilli Sigma Xi Award for his research efforts. Dr. Carraher was the recipient of the 2002 Distinguished Researcher Award from Allied Technologies. In 2016, he was awarded the Distinguished Service Award in Polymer Science by the Polymer Division.



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How to Study Polymers

Studying about polymers is similar to studying any science. Following are some ideas that may assist you as you study.

Much of science is abstract. While much of the study of polymers is abstract, it is easier to conceptualize, make mind pictures, of what a polymer is and how it should behave compared to many other areas of science. For linear polymers, think of a string or rope. Long ropes get entangled with themselves and other ropes. In the same way, polymer chains entangle with themselves and with chains of other polymers that are brought into contact with them. *Thus, create mental pictures of the polymer molecules as you study them.*

Polymers are real and all about us. We can look at giant molecules on a micro or atomic level or on a macroscopic level. The disposable bottles we use may be composed of long chains of poly(ethylene terephthalate [PET]) chains. The aramid tire cord is composed of aromatic polyamide chains. Our hair is made up of complex bundles of fibrous proteins, again polyamides. *The polymers you study are related to the real world in which we live. We experience these “large molecules” at the macroscopic level every day of our lives and this macroscopic behavior is a direct consequence of the atomic-level structure and behavior.* Make pictures in your mind that allow you to relate the atomic and macroscopic worlds.

At the introductory level we often examine only the primary factors that may cause particular giant molecule behavior. Other factors may become important under particular conditions. *The polymer molecules you study at times examine only the primary factors that impact polymer behavior and structure. Even so, these primary factors form the basis for both complex and simple structure–property behavior.*

The structure–property relationships you will be studying are based on well-known basic chemistry and physical relationships. *Such relationships build upon one another and as such you need to study these in an ongoing manner. Understand as you go along. Read the material “before” you go to class.*

This course is an introductory-level course. Each chapter or topic emphasizes knowledge about one or more area. *The science and excitement of polymers has its own language. It is a language that requires you to understand and memorize certain key concepts.* Our memory can be short term or long term. Short-term memory may be considered as that used by an actor or actress for a TV drama. It really does not need to be totally understood, nor retained after the

final “take.” *Long-term memory is required in studying about giant molecules since it will be used repeatedly and is used to understand other concepts (that is, it is built upon).*

In memorizing, learn how you do this best time of day, setting, etc. Use as many senses as necessary, *be active*, read your assignment, write out what is needed to be known, say it, listen to yourself say it. Also, look for patterns, create mnemonic devices, avoid cramming too much into too less a time, practice associations in all directions, and test yourself. *Memorization is hard work.*

While knowledge involves recalling memorized material, to really “know” something involves more than simple recall—it involves *comprehension, application, evaluation, and integration of the knowledge.* Comprehension is the interpretation of this knowledge-making predictions, applying it to different situations. Analysis involves evaluation of the information and comparing it with other information and synthesis has to do with integration of the information with other information.

In studying about giant molecules, consider doing the following:

- *Skim the text “before” the lecture.*
- *Attend the lecture and take notes.*
- *Organize your notes and relate information.*
- *Read and study the assigned material.*
- *Study your notes and the assigned material.*
- *Review and self-test.*

Learning takes time and effort. Study daily, skimming the text and other study material, think about it, visualize key points and concepts, write down important material, make outlines, take notes, study sample problems, etc. All of these help. Some may help you more than others, so focus on these modes of learning, but not at the exclusion of the other aspects.

In preparing for an exam, consider the following:

- *Accomplish the above: DO NOT wait until the day before the exam to begin studying; inculcate good study habits.*
- *Study wisely: Study how YOU study best—time of day, surroundings, etc.*
- *Take care of yourself; get plenty of sleep the night before the exam.*
- *Attend to last-minute details: Is your calculator working, is it the right kind, do I have the needed pencils, review the material once again, etc.*

- *Know what kind of test it will be, if possible, and get copies of old exams if possible; talk to others that might have already had the course.*

During the test

- *Stay cool, DO NOT PANIC.*
- *Read the directions; try to understand what is being asked for.*
- *In an essay or similar exam, work for partial credit; plan your answers.*
- *In a multiple choice or T/F exam, eliminate obviously wrong choices.*

- *Look over the entire exam; work questions that you are sure of, then go to less sure questions; check answers if time permits.*

The study of polymer molecules contains several types of content:

- *Facts:* The term *polymer* means “many” (poly) “units” (mers).
- *Concepts:* Linear polymers are long molecules like a string.
- *Rules:* Solutions containing polymer chains are more viscous, slower flowing, than solutions that do not contain polymers.

Polymer Nomenclature

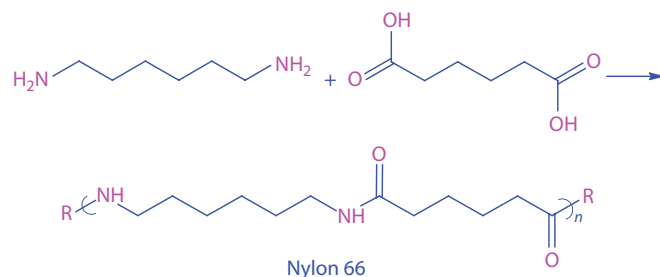
As with most areas, the language of the area is important. Here we will focus on naming polymers with the emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are given when they are covered in Chapter 4 and for nylons in Chapter 5.

The fact that synthetic polymer science grew in many venues before standard nomenclature groups were present to assist in standardization of the naming approach resulted in many popular polymers having several names including common names. Many polymer scientists have not yet accepted the guidelines given by the official naming committee of the International Union of Pure and Applied Chemistry, IUPAC, because the common names have gained such widespread acceptance. Although there is a wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

P.1 COMMON NAMES

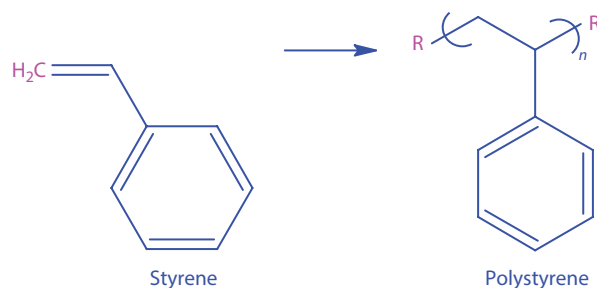
Little rhyme or reason is associated with many of the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasiliensis*—literally “rubber from Brazil”—for natural rubber. Other polymers were named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called nylon 66. Even here, there is no set standard as to how nylon 66 is to be written with alternatives including nylon 66 and nylon 66.



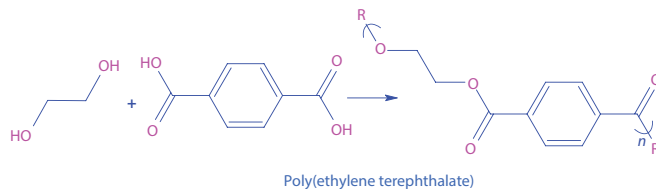
P.2 SOURCE-BASED NAMES

Most common names are source based, that is, they are based on the common name of the reactant monomer, preceded by the prefix “poly.” For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.



The vast majority of polymers based on the vinyl group (H₂C=CHX) or the vinylidene group (H₂C=CX₂) as the repeat unit are known by their source-based names. Thus, polyethylene is the name of the polymer synthesized from the monomer ethylene; poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate.

Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a source-based and a structure-based name.



This polymer is well known by a number of trade names, such as Dacron, its common grouping, polyester, and by the abbreviation PET.

Although it is often suggested that parentheses be used in naming polymers of more than one word, for example, poly(vinyl chloride), but not for single word-polymers, such as polyethylene, some authors entirely omit the use of

parentheses for either case (polyvinyl chloride), so even here a variety of practices exist. In this book, we use parentheses for naming polymers that contain more than one word.

Copolymers are composed of two or more monomers. Source-based names are conveniently used to describe copolymers using an appropriate term between the names of the monomers. Any of a half dozen or so connecting terms may be used, depending on what is known about the structure of the copolymer. When no information is known or intended to be conveyed, the connective term “co” is employed in the general format poly(A-co-B), where A and B are the names of the two monomers. An unspecified copolymer of styrene and methyl methacrylate would be called poly[styrene-co-(methyl methacrylate)].

Kraton, the yellow, rubber-like material often found on the bottom of running shoes, is a copolymer where structural information is known. It is formed from a group of styrene units, that is, a “block” of polystyrene, attached to a group of butadiene units, or a block of polybutadiene, which is attached to another block of polystyrene forming a triblock copolymer. The general representation of such a block might be -AAAAAAABBBBBBAAAAAAAAA-, where each A and B represent an individual monomer unit. The proper source-based name for Kraton is polystyrene-block-polybutadiene-block-polystyrene, or poly-block-styrene-block-polybutadiene-block-polystyrene with the prefix “poly” being retained for each block. Again, some authors will omit the “poly” use giving polystyrene-block-butadiene-block-styrene.

P.3 STRUCTURE-BASED NAMES

Although source-based names are generally employed for simple polymers, IUPAC has published a number of reports for naming polymers. These reports are being widely accepted for the naming of complex polymers. A listing of such names is given in the references section. A listing of source- and structure-based names for some common polymers is given in Table P.1.

P.4 LINKAGE-BASED NAMES

Many polymer “families” are referred to by the name of the particular linkage that connects the polymers (Table P.2). The family name is “poly” followed by the linkage name. Thus, those polymers that contain an ester linkage are known as polyesters, those with an ether linkage are called polyethers, etc.

P.5 TRADENAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe material. They may be used to identify the

TABLE P.1 Source- and Structure-Based Names

Source-Based Names	Structure-Based Names
Polyacrylonitrile	Poly(1-cyanoethylene)
Poly(ethylene oxide)	Polyoxyethylene
Poly(ethylene terephthalate)	Polyoxyethyleneoxyterephthaloyl
Polyisobutylene	Poly(1,1-dimethylethylene)
Poly(methyl methacrylate)	Poly[(1-methoxycarbonyl)-1-methylethylene]
Polypropylene	Poly(1 methylethylene)
Polystyrene	Poly(1-phenylethylene)
Polytetrafluoroethylene	Polydifluoromethylene
Poly(vinyl acetate)	Poly(1-acetoxyethylene)
Poly(vinyl alcohol)	Poly(1-hydroxyethylene)
Poly(vinyl chloride)	Poly(1-chloroethylene)
Poly(vinyl butyral)	Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

TABLE P.2 Linkage-Based Names

Family Name	Linkage	Family Name	Linkage
Polyamide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}-\text{C}- \end{array}$	Polyvinyl	$-\text{C}-\text{C}-$
Polyester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}- \end{array}$	Polyanhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array}$
Polyurethane	$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{O}-\text{C}-\text{N}- \end{array}$	Polyurea	$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \parallel \quad \\ -\text{N}-\text{C}-\text{N}- \end{array}$
Polyether	$-\text{O}-$	Polycarbonate	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{O}-\text{C}-\text{O}- \end{array}$
Polysiloxane	$-\text{O}-\text{Si}-$	Polysulfide	$-\text{S}-$

product of a manufacturer, processor, or fabricator, and may be associated with a particular product or with a material or modified material, or a material grouping. Tradenames (or trade names) are used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the tradename given for the phenol-formaldehyde condensation product developed by Baekeland. A sweater whose contents are described as containing Orlon contains polyacrylonitrile fibers that are “protected” under the Orlon trademark and produced or licensed to be produced by the holder of the Orlon trademark. Carina, Cobex, Dacovin, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all tradenames for poly(vinyl chloride) manufactured by different companies. Some polymers are better known by their tradename than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the tradename held by Dupont.

TABLE P.3 Abbreviations for Selected Polymeric Materials

Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene terpolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET, PETE	Poly(ethylene terephthalate)
PF	Phenyl-formaldehyde	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAI	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile
UF	Urea-formaldehyde		

Abbreviations, generally initials in capital letters, are also employed to describe polymers. Table P.3 contains a listing of some of the more widely used abbreviations and the polymer associated with the abbreviation.

SUMMARY

While there are several important approaches to the naming of polymers, we will use common and source-based names because these are the names that are most commonly used by polymer scientists and the general public, and these names, in particular the source-based

names, allow a good vehicle to convey structure–property relationships.

SELECTED READINGS

- Bikales, N. M. (1987): Nomenclature, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 10, Wiley, NY, p. 191.
- Carraher, C. (2011): *Polymer Chemistry*, 9th ed., CRC Press, Boca Raton, FL.
- Compendium of Macromolecular Nomenclature*, CRC Press, Boca Raton, FL, 1991.
- Jenkins, A.D., Loening, K.L. (1989): Nomenclature, in *Comprehensive Polymer Science*, Vol. 1, Oxford, U.K., pp. 13–54.



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American Chemistry Society Committee on Professional Training Requirements

The recent requirements for accredited programs by the ACS CPT include a polymer component that can be fulfilled by either a course in polymers, which this text fulfills, and/or integration of polymer topics into the foundation courses. The CPT guidelines state the following:

The Committee had lengthy discussions about the possibility of instituting a polymer requirement. “Inclusion of a polymer requirement was under consideration because of the recognition that the properties of large molecules and aggregated systems are different from those of small molecules.... Based on the feedback, the Committee decided that the principles that govern macromolecular, supramolecular, mesoscale, and nanoscale systems must now be part of the curriculum for certified graduates. Furthermore, instruction must cover the preparation, characterization, and physical properties of at least two of the following: synthetic polymers, biological macromolecules, supramolecular aggregates, meso- and/or nanoscale materials. We expect that most departments will meet this requirement through coverage distributed across multiple course required for the certified degree. In that case, the coverage should constitute the equivalent of approximately one-fourth of a standard semester course. An alternative option is to offer a stand-alone course that is required for the certified degree.” This text also supplies material that allows this to occur.

The following gives locations within the text that apply integration of polymer material into each foundational course as well as locations for the other topic areas mentioned in the CPT requirements.

Organic:

- Cpt 5-Step-Reaction sections 1, 4–15
- Cpt 6-Ionic Chain-Reaction sections 3–9
- Cpt 7 Free Radical sections 4–9
- Cpt 8 Copolymerization sections 4–14
- Cpt 15 Synthesis of Reactants and Intermediates for Polymers

Inorganic:

- Cpt 9 Organometallic and Metalloid Polymers
- Cpt 10 Inorganic Polymers (includes nanoscale materials including carbon nanotubes)

Physical:

- Cpt 2 Polymer Structure
- Cpt 3 Molecular Weight
- Cpt 5 Step-Reaction sections 1–4



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Introduction to Polymers

1.1 HISTORY OF POLYMERS

Since most materials are polymeric and most of the recent advances in science and technology involve polymers, some have called this the polymer age. Actually, we have always lived in a polymer age. The ancient Greeks classified all matter as animal, vegetable, and mineral. Minerals were emphasized by the alchemists, but medieval artisans emphasized animal and vegetable matter. All are largely polymeric and are important to life as we know it. Most chemists, biochemists, and chemical engineers are now involved in some phase of polymer science or technology.

The word “polymer” is derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word *macromolecule*, or large molecule, instead of polymer. Others maintain that naturally occurring polymers, or *biopolymers*, and synthetic polymers should be studied in different courses. Others name these large molecules simply “giant molecules.” However, the same principles apply to all polymers. If one discounts the end uses, the differences between all polymers, including plastics, fibers, and elastomers, or rubbers, and natural and synthetic, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, and by the functional groups present, and most of all, by their size allowing an accumulation of these forces.

In addition to being the basis of life itself, protein is used as a source of amino acids and energy. The ancients degraded or depolymerized the protein in meat by aging and cooking, and they denatured egg albumin by heating or adding vinegar to the eggs. Early humans learned how to process, dye, and weave the natural proteinaceous fibers of wool and silk and the carbohydrate fibers from flax and cotton. Early South American civilizations, such as the Aztecs, used natural rubber (*Hevea brasiliensis*) for making elastic articles and for waterproofing fabrics.

There has always been an abundance of natural fibers and elastomers but few plastics. Of course, early humans employed a crude plastic art in tanning the protein in animal skins to make leather and through heating created somewhat “plastic” tortoise shells. They also used naturally occurring tars as caulking materials and extracted shellac from the excrement of small coccid insects (*Coccus lacca*).

Until Wohler synthesized urea from inorganic compounds in 1828, there had been little progress in organic chemistry since the alchemists emphasized the transmutation of base metals to gold and believed in a vital force theory. Despite this essential breakthrough, little progress was made in understanding organic compounds until the 1850s when Kekule developed the presently accepted technique for writing structural formulas. However, polymer scientists displayed a talent for making empirical discoveries before the science was developed.

The original connection between rubber and sulfur is often attributed to Nathaniel Hayward, an American. He is reported to have dusted rubber with sulfur powder and exposed the dusted rubber to sunlight as a way to remove the rubber’s stickiness. Hayward patented his discovery. He turned over his discovery to Charles Goodyear who transformed the connection between sulfur and rubber into the rubber industry.

Charles Goodyear grew up in poverty. He was a Connecticut Yankee born in 1800. He began to work in his father’s farm implements business. Later, he moved to Philadelphia where he opened a retail hardware store that soon went bankrupt. Charles then turned to being an inventor. As a child, he had noticed the magic material that formed a rubber bottle he had found. He visited the

Roxbury India Rubber Company to try and interest them in his efforts to improve the properties of rubber. They assured him that there was no need to do so.

He started his experiments with a malodorous gum from South America in debtor's prison. In a small cottage on the grounds of the prison, he blended the gum, the raw rubber called *Hevea* rubber, with anything he could find—ink, soup, castor oil, etc. While rubber-based products were available, they were either sticky or became sticky in the summer's heat. He found that treatment of the raw rubber with nitric acid allowed the material to resist heat and not to adhere to itself. This success attracted backers who helped form a rubber company. After some effort, he obtained a contract to supply the U.S. Post Office with 150 rubber mailbags. He made the bags and stored them in a hot room while he and his family were away. When they returned, they found the bags in a corner of the room, joined together as a single mass. The nitric acid treatment was sufficient to prevent surface stickiness, but the internal rubber remained tacky and susceptible to heat.

While doing experiments in 1839 at a Massachusetts rubber factory, Charles accidentally dropped a lump of rubber mixed with sulfur on the hot stove. The rubber did not melt but rather charred. He had discovered vulcanization, the secret that was to make rubber a commercial success. While he had discovered vulcanization, it would take several years of ongoing experimentation before the process was really commercially useful. During this time, he and his family were near penniless. While he patented the process, the process was too easily copied and pirated so that he was not able to fully profit from his invention and years of hard work. Even so, he was able to develop a number of items.

Charles Goodyear, and his brother Nelson, transformed natural rubber, *Hevea* rubber, from a heat “softenable” thermoplastic to a less-heat-sensitive product through the creation of cross-links between the individual polyisoprene chainlike molecules using sulfur as the cross-linking agent. *Thermoplastics* are 2D molecules that may be softened by heat. *Thermosets* are materials that are 3D networks that cannot be reshaped by heating. Rather than melting, thermosets degrade. As the amount of sulfur was increased, the rubber became harder becoming a hard rubberlike (ebonite) material.

The spring of 1851 found the construction of a remarkable building on the lawns of London's Hyde Park. The building was designed by a maker of greenhouses so it was not unexpected that it had a “greenhouse look.” This Crystal Palace was to house almost 14,000 exhibitors from all over the world. It was the chance for exhibitors to show their wares. Charles Goodyear, then 50 years old, used this opportunity to show off his over two decades worth of rubber-related products. He decorated his Vulcanite Court with rubber walls, roof, furniture, buttons, toys, carpet, combs, etc. Above it hung a giant six foot rubber raft and assorted balloons. The European public was introduced to the world of new man-made materials.

Within a little more than a decade, Charles Goodyear was dead. Within a year of his death, the American Civil War broke out. The Union military used about \$27 million worth of rubber products by 1865 helping launch the American rubber industry.

In 1862, Queen Victoria, while in mourning for her recently departed husband Albert, opened the world's fair in London. One of the exhibitors was Alexander Parks. He was displeased with the limited colors available for rubber products—generally dull and dark. In his workshop in Birmingham, England, he was working with nitrocellulose, a material made from the treatment of cotton with nitric and sulfuric acids. Nitrocellulose solutions were made from organic liquids such as ethanol and ether. Thin films and coatings were made by simply pouring the nitrocellulose solutions onto the desired item or surface and allowing the solvent to evaporate. He wanted to make solid objects from nitrocellulose. After years of work, he developed a material he called Parkesine from which he made buttons and combs, and in fact many of the items were made of rubber—except that his materials could be brightly colored, clear, or made to shine like mother-of-pearl. At the London world's fair, he advertised “PATENT PARKESINE of various colours: hard elastic, transparent, opaque, and waterproof.” Even with his work he had not developed a material that could be “worked” or was stable and even with his hype, the material never caught on except within exhibition halls.

About this time, John Wesley Hyatt, a printer from Albany, NY, was seeking a \$10,000 prize for anyone who could come up with a material that was a substitute for ivory billiard balls, developed a material that was stable and could be “worked” from shellac and wood pulp. He then turned to nitrocellulose discovering that shredded nitrocellulose could be mixed with camphor, heated

under pressure, to produce a tough white mass that retained its shape. This material, dubbed celluloid, could be made into the usual rubberlike products, but also solid pieces like boxes, wipe-clean linen collars, cuffs, and ping-pong balls. Celluloid could also, like the shellac-wood pulp mixture, be worked—cut, drilled, and sawed. But celluloid was flammable and did not stand up well in hot water. The wearers of celluloid dentures truly could have their “teeth curled” when drinking a hot cup of coffee. One of its best qualities was that it could be made to “look like” other materials—it could be dyed to look like marble and swirled to mimic tortoiseshell and mother-of-pearl and even look and feel like ivory. It did not make good billiard balls. One account has billiard balls hitting and exploding like a shot that caused cowboys to draw their guns.

Both cellulose and cellulose nitrate are linear, or 2D, polymers, but the former cannot be softened because of the presence of multitudinous hydrogen bonds between the chainlike molecules. When used as an explosive, the cellulose nitrate is essentially completely nitrated, but the material used by Parks and Hyatt was a dinitrate, still potentially explosive, but less so. Parks added castor oil and Hyatt added camphor to plasticize—reduce the effect of the hydrogen bonding—the cellulose nitrate allowing it some flexibility.

Worldwide, rubber gained in importance with the invention of the air-filled or pneumatic tires by a Scotsman, John Dunlop in 1888. He had a successful veterinarian practice in Belfast. In his off time, he worked to improve the ride of his son’s tricycle. His invention happened at the right time. The automobile was emerging and the air-filled tires offered a gentler ride. Thus, was begun the tire industry.

All of these inventions utilized natural materials as at least one ingredient. After years of work in his chemistry labs in Yonkers, NY, Leo Baekeland in 1907 announced in an American Chemical Society meeting the synthesis of the first truly synthetic polymeric material latter dubbed Bakelite.

Baekeland was born in Belgium in 1863, the son of an illiterate shoe repairman and a maid. He was bright and received, with highest honors, his doctorate at the age of 20. He could have spent the remaining part of his life in academics in Europe, but heading the words of Benjamin Franklin, he sailed to America. In the 1890s, he developed the first photographic paper, called Velox, which could be developed in synthetic light rather than sunlight. George Eastman saw the importance of this discovery and paid Baekeland \$750,000 for the rights to use this invention.

It was generally recognized by the leading organic chemists of the nineteenth century that phenol would condense with formaldehyde. Since they did not recognize the concept of functionality, Baeyer, Michael, and Kleeberg produced useless cross-linked goos, gunks, and messes and then returned to their research on reactions of monofunctional reactants. However, by the use of a large excess of phenol, Smith, Luft, and Blumer were able to obtain a hard, but meltable thermoplastic material.

With his \$750,000, Baekeland set up a lab next to his home. He then sought to solve the problem of making the hard material made from phenol and formaldehyde soluble. After many failures, he thought about circumventing the problem by placing the reactants in a mold of the desired shape and allowing them to form the intractable solid material. After much effort, he found the conditions under which a hard, clear solid could be made—Bakelite was discovered. Bakelite could be worked, it was resistant to acids and organic liquids, stood up well to heat and electrical charge, and could be dyed to give colorful products. It was used to make bowling balls, phonograph records, telephone housings, gears, and cookware. His materials also made excellent billiard balls. Bakelite also acted as a binder for sawdust, textiles, and paper forming a wide range of composites including Formica laminates, many of which are still used. It was also used as an adhesive giving us plywood.

While there is no evidence that Baekeland recognized what polymers were, he appeared to have a grasp on functionality and how to “use” it to produce thermoplastic materials that could later be converted to thermosets. Through control of the ratio of phenol to formaldehyde, he was able to form a material that was a thermoplastic. He coined the term “A-stage resole resin” to describe this thermoplastic. This A-stage resole resin was converted to a thermoset cross-link, C-stage *Bakelite*, by additional heating. Baekeland also prepared thermoplastic resins called “novolacs” by the condensation of phenol with a lesser amount of formaldehyde under acidic conditions. The thermoplastic novolacs were converted to thermosets by addition of more formaldehyde. While other polymers had been synthesized in the laboratory using a combination of chemicals and

naturally derived materials, Bakelite was the first truly synthetic plastic. The “recipes” used today differ little from the ones developed by Baekeland showing his ingenuity and knowledge of the chemistry of the condensation of the trifunctional phenol and difunctional formaldehyde.

While poly(vinyl chloride) was initially formed by Baumann in 1872, it awaited interest until 1926 when B. F. Goodrich discovered how to make sheets and adhesives from poly(vinyl chloride), and the “vinyl-age” began. While polystyrene was probably first formed by Simon in 1839, it was almost 100 years later, 1930, that the German giant company I. G. Farben placed polystyrene on the market. Polystyrene molded parts became common place. Rohm and Haas bought out plexiglass from a British firm in 1935 and began the production of clear plastic parts and goods including replacements for glass as camera lenses, aircraft windows, clock faces, and car taillights.

To this time, polymer science was largely empirical, instinctive, and intuitive. Prior to World War I, celluloid, shellac, Galalith (casein), Bakelite, and cellulose acetate plastics; *Hevea* rubber, cotton, wool, and silk rayon fibers; Glyptal polyester coatings; bitumen or asphalt; and coumarone-indene and petroleum resins were all commercially available. However, as evidenced by the chronological data shown in Table 1.1, there was little additional development in polymers prior to World War II because of a general lack of fundamental knowledge of polymers. But the theoretical basis was being built. Only a few of many giants will be mentioned.

Over a century ago, Graham coined the term “colloid” for aggregates with dimensions in the range of 10^{-9} to 10^{-7} m. Unfortunately, the size of many macromolecules is in this range, but it is important to remember that unlike colloids, whose connective forces are ionic and/or secondary forces, polymers are individual molecules whose size cannot be reduced without breaking the covalent bonds that hold the atoms together. In 1860, an oligomer, a small polymer, was prepared from ethylene glycol and its structure correctly given as $\text{H}-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$. But when poly(methacrylic acid) was made by Fittig and Engelhorn in 1880, it was incorrectly assigned a cyclic structure. Polymers were thought of as being colloids or cyclic compounds like cyclohexane. By the use of the Raoult and van't Hoff molecular weight concepts, several scientists obtained high-molecular-weight values for these materials and for a number of other polymeric materials. But since the idea of large molecules was not yet accepted, they concluded that these techniques were not applicable to these molecules rather than accepting the presence of giant molecules.

The initial “tire-track in the sand” with respect to tires was the discovery of vulcanization of rubber by Charles Goodyear in 1844. The first rubber tires appear in the mid-1880s. These tires were solid rubber with the rubber itself absorbing the bumps and potholes. John Dunlop invented the first practical pneumatic or inflatable tire with his patent granted in 1888. Andre Michelin was the first person to use the pneumatic tire for automobiles. The Michelin brothers, Andre and Edouard, equipped a racing car with pneumatic tires and drove it in the 1895 Paris–Bordeaux road race. They did not win but it was sufficient advertising to begin interest in pneumatic tires for automobiles. Further, because they did not cause as much damage to the roads, pneumatic tires were favored by legislation. It is interesting to see that the names of these three pioneers still figure prominently in the tire industry. Even so, another inventor Thompson had actually been given the first patent for a vulcanized rubber pneumatic tire in 1845, but it did not take off. Thompson was a prolific inventor also having patented a fountain pen in 1849 and a steam traction engine in 1867.

A number of the giant tire companies started at the turn of the century. In America, many of these companies centered about Akron, the capital of the rubber tire. In 1898, the Goodyear Tire and Rubber Company started. The Firestone Tire and Rubber Company was started by Harvey Firestone in 1900. Other tire companies shortly followed.

Hermann Staudinger studied the polymerization of isoprene as early as 1910 (Picture 1.1). Intrigued by the difference between this synthetic material and natural rubber, he began to focus more of his studies on such materials. His turn toward these questionable materials, of interest to industry but surly not academically important, was viewed unkindly by his fellow academics. He was told by one of his fellow scientists, “Dear Colleague, Leave the concept of large molecules well alone... There can be no such thing as a macromolecule.”

Staudinger systematically synthesized a variety of polymers. In the paper *Über Polymerization* in 1920, he summarized his findings and correctly proposed linear structures for such important polymers as polyoxymethylene and polystyrene. X-ray studies of many natural and synthetic

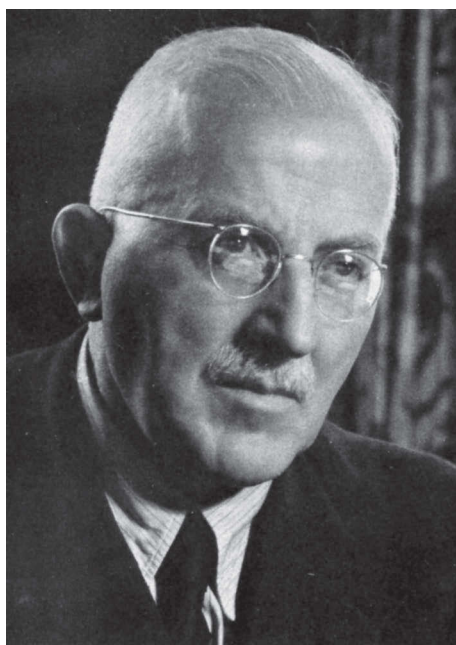
TABLE 1.1 Chronological Developments of Commercial Polymers (to 1992)

Before 1800	Cotton, flax, wool, and silk fibers; bitumens caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); and natural rubber (<i>Hevea brasiliensis</i>), gutta-percha, balata, and shellac
1839	Vulcanization of rubber (Charles Goodyear)
1845	Cellulose esters (Schonbein)
1846	Nitration of cellulose (Schonbein)
1851	Ebonite (hard rubber; Nelson Goodyear)
1860	Molding of shellac and gutta-percha
1868	Celluloid (plasticized cellulose nitrate; Hyatt)
1888	Pneumatic tires (Dunlop)
1889	Cellulose nitrate photographic films (Reichenbach)
1890	Cuprammonia rayon fibers (Despeisses)
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)
1903	First tubeless tire (Litchfield of Goodyear Tire Co.)
1897	Poly(phenylene sulfide)
1901	Glyptal polyesters
1907	Phenol-formaldehyde resins (Bakelite; Baekeland)
1908	Cellulose acetate photographic fibers
1912	Regenerated cellulose sheet (cellophane)
1913	Poly(vinyl acetate)
1914	Simultaneous interpenetrating network
1920	Urea-formaldehyde resins
1923	Cellulose nitrate automobile lacquers
1924	Cellulose acetate fibers
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) wall covering
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers, DuPont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea-formaldehyde resins
1930	Polyethylene (Friedrich/Marvel)
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprene elastomer (Neoprene; Carothers)
1934	Epoxy resins (Schlack)
1935	Ethyl cellulose
1936	Poly(vinyl acetate)
1936	Poly(vinyl butyral) (safety glass)
1937	Polystyrene
1937	Styrene-butadiene (Buna-S) and styrene-acrylonitrile (Buna-N) copolymer elastomers
1939	Melamine-formaldehyde resins
1939	Nylon 6 (Schlack)
1939	Nitrile rubber (NR)
1940	Isobutylene-isoprene elastomer (butyl rubber; Sparks and Thomas)
1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET)
1942	Butyl rubber
1942	Unsaturated polyesters (Ellis and Rust)
1943	Fluorocarbon resins (Teflon; Plunket)
1943	Silicones
1945	SBR
1946	Polysulfide rubber (Thiokol)
1948	Copolymers of acrylonitrile, butadiene, and styrene (ABS)

(Continued)

TABLE 1.1 (Continued) Chronological Developments of Commercial Polymers (to 1992)

1949	Cyanoacrylate (Goodrich)
1950	Polyester fibers (Winfield and Dickson)
1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High-impact polystyrene (HIPS)
1953	Polycarbonates (Whinfield & Dickson)
1956	Poly(phenylene ether); Poly(phenylene oxide) (GE)
1957	High-density polyethylene (HDPE)
1957	Polypropylene
1957	Polycarbonate
1958	Poly(dihydroxymethylcyclohexyl terephthalate) (Kodel, Eastman Kodak)
1960	Ethylene-propylene copolymer elastomers
1961	Aromatic nylons (Aramids, Nomex, DuPont)
1962	Polyimide resins
1964	Poly(phenylene oxide)
1964	Ionomers
1965	Polysulfone
1965	Styrene-butadiene block copolymers
1966	Liquid crystals
1970	Poly(butylene terephthalate)
1974	Polyacetylene
1982	Polyetherimide (GE)
1991	Carbon nanotubes (Iijima; NEC Lab)

**PICTURE 1.1** Herman Staudinger, Father of Polymer Science. (From Wikipedia.)

materials were used as structural proof that polymers existed. Foremost in these efforts were Herman Mark and Linus Pauling. Both of these giants contributed to other important areas of science. Pauling contributed to the fundamental understanding of bonding and the importance of vitamins. Mark helped found the academic and communication (journals, short courses, workshops) basis that would allow polymers to grow from its very diverse roots.

Probably, the first industrial effort aimed at basic or fundamental research in the chemical sciences was by DuPont. Their initial venture in artificial fibers was in 1920 when they purchased a 60% interest in Comptoir des Textiles Artificiels, a French rayon company. The combined company was named the DuPont Fiber Company. DuPont spent considerable effort and money on expanding the properties of rayon. In 1926, Charles M. A. Stine, director of the chemical department, circulated a memo to DuPont's executive committee suggesting that the company move from investing in already existing materials to investigating new materials. This was a radical idea that a company supposedly focused on profit spend some of its effort on basic research. The executive committee approved much of Stine's proposal giving him \$25,000 a month for the venture allowing him to hire 25 chemists for the task. The initial hiring was difficult because academic chemists did not trust DuPont to allow them to do basic research. A year later, he was able to make his central hiring, Wallace Hume Carothers.

Wallace Hume Carothers is the father of synthetic polymer science (Picture 1.2). History is often measured by the change in the flow of grains of sand in the hour glass of existence. Carothers is a granite boulder in this hour glass. Carothers was born, raised, and educated in the Midwest of the United States. In 1920, he left Tarkio College with his BS degree and entered the University of Illinois where he received his MA in 1921. He then taught at the University of South Dakota where he published his first paper. He returned to receive his PhD under Roger Adams in 1924. In 1926, he became an instructor in organic chemistry at Harvard.

In 1927, the DuPont Company reached a decision to begin a program of fundamental research "without any regard or reference to commercial objectives." This was a radical departure since the bottom line was previously products marketed and not papers published. Charles Stine, director of DuPont's chemical department, was interested in pursuing fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer formation and convinced the Board to hire the best chemists in each field to lead this research. Stine visited with many in the academic community including then president of Harvard, one of my uncles, J.B. Conant, an outstanding chemist himself, who told him about Carothers. Carothers was persuaded to join the DuPont group attracted by a generous research budget and an approximate doubling of his academic salary to \$6000. This was the birth of the Experimental Station at Wilmington, Delaware.

Up to this point, it was considered that universities were where discoveries were made and industry was where they were put to some practical use. This separation between basic and applied



PICTURE 1.2 Wallace Hume Carothers, one of the pioneers of polymer science. (From Wikipedia.)

work was quite prominent at this juncture and continues in many areas even today in some fields of work though the difference has decreased. But in polymers, most of the basic research was done in industry having as its inception the decision by DuPont to bridge this “unnatural” gap between fundamental knowledge and application. In truth, they can be considered as the two hands of an individual and in order to do manual work both hands are important.

Staudinger believed that large molecules were based on the jointing, through covalent bonding, of large numbers of atoms. Essentially, he and fellow scientists like Karl Freudenberg, Herman Mark, Michael Polanyi, and Kurt Myer looked at already existing natural polymers. Carothers, however, looked at the construction of these giant molecules from small molecules forming synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to “investigate how the properties of these substances depended on constitution.” Early work included the study of polyester formation through reaction of diacids with diols forming polyesters. But he could not achieve molecular weights greater than about 4000 below the size where many of the interesting so-called polymeric properties appear.

DuPont was looking for a synthetic rubber. Carothers assigned Arnold Collins to this task. Collins’ initial task was to produce pure divinylacetylene. While performing the distillation of an acetylene reaction, in 1930, he obtained a small amount of an unknown liquid that he set aside in a test tube. After several days, the liquid turned to a solid. The solid bounced and eventually was shown to be a synthetic rubber polychloroprene whose properties were similar to those of vulcanized rubber but it was superior in its resistance to ozone, ordinary oxidation, and to most organic liquids. It was sold under its generic name “neoprene” and the trade name “Duprene.”

As you read through this book, you will see that there were many so-called “accidental” discoveries. But as Louis Pasteur wrote “In the fields of observation, chance favors only the mind that is prepared.” So while results from a given experiment may be unexpected, we are able to profit from them only as far as we are prepared to look at the significance of the observation and place it in context with other knowledge, that is, the prepared mind.

Also in 1930, Carothers and Julian Hill designed a process to remove water that was formed during the esterification reaction. Essentially, they simply froze the water as it was removed using another recent invention called a molecular still (basically a heating plate coupled to vacuum) allowing the formation longer chains. In April, Hill synthesized a polyester using this approach and touched a glass stirring rod to the hot mass and then pulled the rod away effectively forming strong fibers, the pulling helping reorient the somewhat mobile polyester chains. The polyester had a molecular weight of about 12,000. Additional strength was achieved by again pulling the cooled fibers. Further reorienting occurred. This process of “drawing” or pulling to produce stronger fibers is now known as “cold drawing” and is widely used in the formation of fibers today. The process of “cold drawing” was discovered by Carothers’ group. While interesting, the fibers were not considered to be of commercial use. Carothers and his group then moved to look at the reaction of diacids with diamines instead of diols. Again, fibers were formed but these initial materials were deemed not to be particularly interesting.

In 1934, Paul Flory was hired to work with Carothers to help gain a mathematical understanding of the polymerization process and relationships. Thus, there was an early association between theory and practice or structure–property relationships.

In 1934, Donald Coffman, a member of the Carothers team, pulled a fiber from an aminoethyl-ester (polyamide) polymer. The fiber retained the elastic properties of the polyesters previously investigated but had a higher melting point sufficiently high as to allow clothing made from it to be laundered and ironed. The field of candidates for further investigation was narrowed to two-polyamide 5,10 made from 1,5-pentamethylene diamine and sebacic acid, and polyamide 6,6 synthesized from 1,6-hexamethylenediamine and adipic acid. Polyamide 6,6 won because the monomers could be made from benzene, a readily available feedstock from coal tar.

The polyamide fiber project was begun in earnest using the reaction of adipic acid with hexamethylenediamine. They called the polyamide fiber 66 because each carbon-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melt temperature. DuPont chose this material for production. These polyamides were given the name “nylons.” Thus, was born nylon 66. It was the first synthetic material whose properties equaled or exceeded the natural analog, namely, silk. (In reality, this may not be the truth, but at the time, it was believed to be true.)

The researchers had several names for polyamide 6,6 including rayon 66, fiber 66, and Duparon derived from “Dupont pulls a rabbit out [of] the hat nitrogen/nature/nature/nozzle/naphtha.” The original “official” name was “Nuron” that implied newness and also spelled “on run” somewhat backward. This name was too close to other trademarked names and was renamed “Norton” and eventually to what we know today as “Nylon.”

As women’s hemlines rose in the 1930s, silk stockings were in great demand but were very expensive. Nylon changed this. Nylon could be woven into sheer hosiery. The initial presentation of nylon hose to the public was by Stine at a forum of women’s club members in New York City on October 24, 1938. Nearly 800,000 pairs were sold on May 15, 1940, alone—the first day they were on the market. By 1941, nylon hosiery held 30% of the market but by December 1941, nylon was diverted to make parachutes, etc.

From these studies, Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials, namely, primary covalent bonds. Many of the polymer chemistry names and ideas that permeate polymer science today were standardized through his efforts.

America is a melting pot for immigrants and during World War II, it profited from the immigration of a number of scientists including Herman Mark. Because of over 5 years of service as a combat soldier in the elite k.k. Kaiserschutzen Regiment Nr. II Imperial Austrian Army during World War I, Mark did not receive his PhD until the age of 26 in 1919. He was highly decorated and the Austrian hero of the Battle of Mount Ortigara in 1917. He accepted a position at the University of Berlin with many other well-known chemists including Max Bergmann, Hermann Leuchs, Emil Fisher, and Carl Harries. He moved to industry becoming head of research in a division of I. G. Farben.

When the Nazis came to power, he moved to Austria. Though Lutheran, Mark was of Jewish decent so by early 1938 began planning to leave Austria. He started converting his wealth into platinum wire which he made into hangers. His wife knitted hanger covers. When Hitler’s troops invaded Austria, he was stripped of his passport. He retrieved the passport through a bribe and obtained a visa to visit Canada. In April 1938, he mounted a Nazi flag on the radiator of their car, strapped ski equipment onto the car’s roof, and drove across the border. Supposedly, he was asked by a border guard if he had any wealth to declare. He replied that he had only the clothes on his back and the hangers upon which they hung. From Zurich, he traveled to France, then England, and then Canada and finally the United States where he joined the Brooklyn Polytechnic.

While at Brooklyn Polytechnic, he consulted for DuPont and was involved in much of the pioneering work that occurred there. His students included many polymer pioneers including Turner Alfrey, Paul Doty, Isidor Fankuchen, Arthur Tobolsky, W. Hohenstein, and Bruno Zimm. During the war, regular meetings of the chemistry community were organized at Brooklyn Poly focusing mainly on polymers but allowing communication to occur between the academic and industrial scientists. During the war, he worked with the military on a number of projects including creation of a land and sea vehicle, and the use of icebergs to transport large amounts of cargo past the German U-Boats. His first course at Brooklyn Poly was “general polymer chemistry” that attracted many local industrial scientists. He started the long-running Interscience (Wiley) book series on polymers as well as the *Journal of Polymer Science*, again with Wiley. The Institute of Polymer Research was started in 1946 with the creation of a letterhead and located in a vacant razor blade factory.

He worked on x-ray diffraction and Linus Pauling learned x-ray diffraction from Mark leading to Pauling’s seminal work on protein structure. He worked with Albert Einstein using the powerful x-ray tubes available to Mark to verify the Compton effect that provided confirmation of Einstein’s light quantum theory.

In the 1950s and 1960s, he was famous for volunteering to give talks at various colleges about the country showing up with a suitcase and lots of enthusiasm. He was the missionary for polymers.

Representing the true multidisciplinary nature of polymers, early important contributions were also made by physicists, engineers, and those from biology, medicine, and mathematics including W. H. Bragg, Peter Debye, Albert Einstein, and R. Simha.

World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that even excelled currently available materials. Polycarbonate (Kevlar), which could stop a “speeding bullet,” was developed as was polytetrafluoroethylene (Teflon) that was super slick. New materials were developed spurred on by the needs of the military, electronics industry, food industry, etc. The creation of new materials continues today at an even accelerated pace brought on by the need for materials with specific properties and the growing ability to tailor—make giant molecules, macromolecules—polymers.

Unlike other areas of chemistry, most of the basic research has been done in industry so that there is often a close tie between discoveries and their commercialization. Table 1.2 lists some of the dates of commercialization for some important synthetic polymer discoveries.

A number of Nobel Prizes have been given for polymer work. Table 1.3 contains winners whose efforts are related to synthetic polymers. In truth, there are many more since most of the prizes given out in medicine and biology deal with giant molecules.

There are also a number of Nobel Prizes given for advances contributing to polymers. The 2010 Nobel Prize in chemistry was given to Richard Heck, Ei-ichi Negishi, and Akira Suzuki for their work on palladium-catalyzed cross-coupling reactions employed to synthesize pi-conjugated oligomers, dendrimers, and polymers.

Throughout this text, advances are placed in some historical setting. This adds some texture to the topics as well as acting as case histories that are widely used in subject areas such as business and medicine.

TABLE 1.2 Commercialization of Selected Polymers

Polymer	Year	Company
Bakelite	1909	General Bakelite Corp.
Rayon	1910	American Viscose Company
Poly(vinyl chloride)	1927	Goodrich
Styrene-butadiene copolymer	1929	I.G. Farben
Polystyrene	1929/1930	I.G. Farben & Dow
Neoprene	1931	DuPont
Poly(methyl methacrylate)	1936	Rohm & Haas
Nylon 66	1939/1940	DuPont
Polyethylene (LDPE)	1939	ICI
Poly(dimethyl siloxane)	1943	Dow Corning
Acrylic fiber	1950	DuPont
Poly(ethylene terephthalate), PET	1953/1954	DuPont/ICI
Polyurethane block copolymers (Spandex)	1959	DuPont
Poly(phenylene terephthalamide)	1960	DuPont

TABLE 1.3 Nobel Prize Winners for Their Work with Synthetic Polymers

Scientist(s)	Year	Area
Herman Staudinger	1953	Polymer hypothesis
Karl Ziegler and Giulio Natta	1963	Stereoregulation of polymer structure
Paul Flory	1974	Organization of polymer chains
Bruce Merrifield	1984	Synthesis on a solid matrix
Pierre de Gennes	1991	Polymer structure and control at interfaces
A. J. Heeger, Alan MacDiarmid, and H. Shirakawa	2000	Conductive polymers
Y. Chauvin, R. H. Grubbs, and R.R. Schrock	2005	Metathesis
R. Heck, E. Negishi, and A. Suzuki	2010	Palladium-catalyzed cross-coupling reactions

1.2 WHY POLYMERS?

Polymers are all about us. They serve as the very basis of both plant and animal life as proteins, nucleic acids, and polysaccharides. In construction, they serve as the basic building blocks as concrete, insulation, and wooden and composite beams. At home, they are found as the materials for our rugs, curtains, coatings, wastepaper baskets, water pipes, window glass, ice cube trays, and pillows. In transportation, they are present in ever-increasing amounts in our aircraft, automobiles, ships, and trucks. In communication, they form critical components in our telephones, TVs, computers, CDs, newspaper, optical fibers, and cell phones. Plastics act as favorite materials for our toys such as toy soldiers, plastic models, toy cars, dolls, skip ropes, hula hoops, and corvettes. Our food is polymer intense as meats, vegetables, breads, and cookies. In history, polymers have been the vehicle for the Magna Carta, Torah, Bible, Koran, and our Declaration of Independence. Outside our homes, they are present in our flowers, trees, soil, spider webs, and beaches. In fact, it is improbable that a polymer is not involved in your present activity—reading a paper book, holding a plastic-intense writing device, sitting on a cloth-covered chair or bed, and if your eyes need corrective vision, glasses, and contact lenses of one variety or another.

Polymers gain their importance because of their size. Many polymers are made from inexpensive and readily available materials allowing vast quantities of products to be made for a high increase in value, but they are typically inexpensive compared to nonpolymer alternatives. They also often have desirable physical and chemical properties. Some polymers are stronger on a weight basis than steel. Most are resistant to rapid degradation and rusting. You will learn more about these essential materials for life and living in this text.

Polymers are often divided according to whether they can be melted and reshaped through application of heat and pressure. These materials are called “**thermoplastics**.” The second general classification belongs to compounds that decompose before they can be melted or reshaped. These polymers are called “**thermosets**.” While both thermoset and thermoplastic polymers can be recycled, because thermoplastics can be reshaped simply through application of heat and pressure, recycling of thermoplastics is easier and more widespread.

In general groups, synthetic polymers are often described by their “use” and “appearance” as fibers, elastomers, plastics, adhesives, and coatings. A common toothbrush illustrates the three major physical forms of synthetic polymers—the rubbery (elastomeric) grips, plastic shaft, and fibrous bristles. The rubbery grips have a relatively soft touch; the plastic shaft is somewhat flexible and hard; and the bristles are highly flexible. Another illustration of the breath of polymers about us is given in Table 1.4 where polymers are divided according to source.

To get an idea of the pervasiveness of polymers in our everyday life, we can look at containers. Most containers are polymeric—glass, paper, and synthetic polymer. It is relatively easy to identify each of these general categories. Even, within the synthetic polymer grouping, it has become relatively easy to identify the particular polymer used in some applications such as with disposable containers. Most of these synthetic polymers are identified by an “identification code” that is imprinted somewhere on the plastic container, generally on their bottom. The numbers and letters are described in Figure 1.1. The recycling code was developed by the Society of Plastics Industry for use with containers. Today, the “chasing arrows” triangle is being used more widely for recycling by the public. A colorless somewhat hazy water container has a “2” within the “chasing” arrows and underneath it “HDPE” both indicating the bottle is made of high-density polyethylene. The clear, less flexible soda bottle has a “1” and “PETE” both signifying that the container is made out of poly(ethylene terephthalate), a polyester. A brownish clear medicine or DVD container has a “5” and the letters “PP” on its bottom conveying the information that the bottle is made of polypropylene (Picture 1.3). Thus, ready identification of some common items is easy.

But because of the use of many more complex combinations of polymers for many other items, such identification and identification schemes are not as straightforward. For some items, such as clothing and rugs, labels are present that tell us the major materials in the product. Thus, a T-shirt might have “cotton” on its label signifying that the T-shirt is largely made of cotton. A dress shirt’s label may say 55% cotton and 45% polyester meaning it is made from two polymers. Some items are identified by trade names. Thus, a dress advertised as being made from Fortrel (where “Fortrel” is a trade name) means it is made largely of a polyester material, probably the same

TABLE 1.4 Common Polymers

Material/Name	Typical Polymer	Chapters
Styrofoam	Polystyrene	7
PVC pipe	Poly(vinyl chloride)	7
Nylon stockings	Polyamide, Nylon 66	5
Concrete	Cement	10
Meat	Protein	4
Plexiglass	Poly(methyl methacrylate)	7
Automotive bumpers/side panels	Polyethylene and polyethylene/polypropylene blends	6 and 8
Potatoes	Starch	4
Compact discs (case)	Polycarbonate (polystyrene)	5
Hula Hoop	Polypropylene, polyethylene	6
Diamond	Carbon	10
Silicon sealants	Polydimethylsiloxane	9
Bakelite	Phenol-formaldehyde cross-linked	5
Super glue	Poly(ethyl cyanoacrylate)	16
Cotton T-shirt	Cellulose	4
Fiberglass	Composite	14
Saran wrap	PVC copolymer	8
Velcro	Polyamide	5
Rubber band	Natural rubber	4
Soda bottle	Poly(ethylene terephthalate), PET	5
Teflon	Polytetrafluoroethylene	7
Orlon sweater	Polyacrylonitrile	7
Sand	Silicon dioxide	10
Pillow stuffing	Polyurethane	5
Wood, paper	Cellulose	4
Human genome	Nucleic acids	4

polyester (PET or PETE) that our soda bottle is made from. Some everyday items are a complex of many materials only some or none noted. This is true for many running shoes and tires. Tires will often be described as being polyester (again, probably the same PETE) or nylon (or aramid). This describes only the composition of the tire cord but does not tell us what other materials are included in the tire's composition. Yet those that deal with tires generally know what materials are used in the manufacture of the tire in addition to the "stated ingredients." You will be introduced, gently, to the identification of the main polymers that are present in many everyday items, either through looking at labels, researching on the web, simply knowing what certain items are generally composed of, through the feel and gross physical properties (such as flexibility and stiffness) of the material, etc.

Further, the properties of essentially the same polymer can be varied through small structural changes giving materials with different properties and uses. There is a match between desired properties and the particular material used. For instance, for plastic bags, strength and flexibility are needed. The bag material should be somewhat strong, inexpensive (since many bags are "throwaway" items), and readily available in large quantities. Increased strength is easily gained from increasing thickness. But with increased thickness comes decreased flexibility, increased cost since more material is needed to make the thicker bags, and increased transportation (because of the additional weight) and storage costs. Thus, there is a balance between many competing factors. Plastic bags are typically made from three polymers, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) (actually a copolymer with largely ethylene units). These different polyethylene polymers are similar differing only in the amount of branching that results in differing tendencies to form ordered (crystalline) and less ordered (amorphous) chain arrangements. You will learn more about them in Chapter 6. Grocery bags are generally made from HDPE, which is largely a linear polymer that








	<p>Poly(ethylene terephthalate)—PET or PETE</p> <p>PET is the plastic used to package the majority of soft drinks. It is also used for some liquor bottles, peanut butter jars, and edible-oil bottles. About one-quarter of plastic bottles are PET. PET bottles can be clear; they are tough and hold carbon dioxide well.</p>
	<p>High-density polyethylene—HDPE</p> <p>HDPE is a largely linear form of polyethylene. It accounts for over 50% of the plastic bottle market and is used to contain milk, juices, margarine, and some grocery snacks. It is easily formed through application of heat and pressure and is relatively rigid and low cost.</p>
	<p>Poly(vinyl chloride)—PVC or V</p> <p>PVC is used “pure” or as a blend to make a wide variety of products including PVC pipes, food packaging film, and containers for window cleaners, edible oils, and solid detergents. It accounts for only 5% of the container market.</p>
	<p>Low-density polyethylene—LDPE</p> <p>LDPE has branching and is less crystalline, more flexible, and not as strong as HDPE. The greater amount of amorphous character makes it more porous than HDPE, but it offers a good inert barrier to moisture. It is a major material for films from which trash bags and bread bags are made.</p>
	<p>Polypropylene—PP</p> <p>PP has good chemical and fatigue resistance. Films and fibers are made from it. Few containers are made of PP. It is used to make some screw-on caps, lids, yogurt tubs, margarine cups, straws, and syrup bottles.</p>
	<p>Polystyrene—PS</p> <p>PS is used to make a wide variety of containers, including those known as “Styrofoam” plates, dishes, cups, etc. Cups, yogurt containers, egg cartons, meat trays, and plates are made from PS.</p>
	<p>Other plastics</p> <p>A wide variety of other plastics are coming to the marketplace including copolymers, blends, and multilayered combinations.</p>

FIGURE 1.1 The Society of Plastics Industry recycling codes utilizing the numbers 1–7 and bold, capital letters to designate the material utilized to construct the container.



PICTURE 1.3 Chasing arrows and number for the top of a DVD container made from polypropylene.

has a high degree of crystallinity. Here, in comparison to LDPE film with the same strength, the bags are thinner allowing a decrease in cost of materials, transportation cost, and storage space. The thinness allows good flexibility. LDPE is used for dry cleaning garment bags where simply covering the garments is the main objective rather than strength. The LDPE is less crystalline and weaker, but more flexible, because of the presence of more branching in comparison to HDPE. The thicker glossy shopping bags from malls are often LLDPE, which, like HDPE, is largely linear. This increased thickness results in the bags being less flexible. These bags can be used many times.

Thus, most of the common items about us are polymeric. Table 1.4 gives a brief listing of some of these materials along with the locations where they will be dealt with in the book.

With the electronic age we can access the web to gather lots of general information about most of the topics including polymers. This book allows you to have a greater appreciation and understanding of such information and the products about us, including our own bodies.

1.3 TODAY'S MARKETPLACE

As noted earlier, polymers are all around us. Over 100 billion pounds (50 million tons) of synthetic polymers is produced annually in the United States (Tables 1.5 through 1.9), and the growth of the industry is continuing at a fast rate. There is every reason to believe that this polymer age will continue as long as petroleum and other feedstocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 100 billion pounds of synthetic polymers consumed each year in the United States translates to over 300 pounds for every man, woman, and child in the United States. This does not include paper and wood-related products (Table 1.10; over 500 pounds/person/year), natural polymers such as cotton and wool, or inorganic polymers (Table 1.11).

Polymers are all about us. The soils we grow our foods from are largely polymeric as are the foods we eat. The plants about us are largely polymeric. We are walking exhibitionist as to the widespread nature of polymers—from our hair and finger nails, our skin, bones, tendons, and muscles; our clothing like socks, shoes, glasses, undergarments; the morning newspaper; major amounts of our automobiles, airplanes, trucks, boats, and spacecraft; our chairs, wastepaper baskets, pencils,

TABLE 1.5 U.S. Production of Plastics (Millions of Pounds; 2013)

<i>Thermosetting resins</i>	
Epoxies	500
Ureas, melamines, and phenolics; Misc.	14,500
Total	15,000
<i>Thermoplastics</i>	
<i>Polyethylenes</i>	
Low density	7,000
High density	17,900
Linear low density	13,900
Polypropylene	16,400
<i>Polystyrene</i>	
Polystyrene	4,500
Acrylonitrile-butadiene-styrene and styrene-acrylonitrile	2,600
Polyamides, nylons	1,200
Poly(vinyl chloride) and copolymers	15,400
Other thermoplastics	15,400
Total thermoplastics	93,000
<i>Grand total</i>	108,000

Source: American Chemistry Council, Washington, DC.

TABLE 1.6 Thermoplastic Sales by Major Market (Millions of Pounds; 2013)

Transportation	2,800
Building and construction	12,200
Furniture and furnishings	1,500
Electrical and electronic	1,700
Packaging	25,700
Industrial and machinery	850
Adhesives, inks, and coatings	350
Consumer and institutional	15,000
Other	1,300
Exports	14,200
Total	75,700

Source: American Chemistry Council, Washington, DC.

TABLE 1.7 U.S. Production of Man-Made Fibers (Millions of Pounds; 2014)

<i>Noncellulosic</i>	
Nylons	1300
Olefins	2200
Polyesters	2900
<i>Cellulosic</i>	
Acetate	55
Lyocell (rayon)	120

Source: Fiber Economics Bureau, Arlington, VA.

TABLE 1.8 U.S. Coatings Consumption (Billion Dry Pounds; 2015; Estimated)

Year	1996	2001	2006	2011	2015
<i>Consumption by segment</i>					
Architectural	3.6	3.9	4.9	3.9	4.5
Original equipment manufacturers	2.1	2.3	2.4	1.0	2.2
Special purpose	1.8	2.0	2.2	2.0	2.1
Total	7.5	8.2	9.5	7.8	8.8
<i>Consumption by technology</i>					
Water-based					
Architectural	2.8	3.0	3.8	3.1	3.7
Industrial	0.9	1.1	1.4	1.3	1.4
Solvent-based					
Architectural	0.9	0.9	1.2	0.8	0.8
Industrial	2.3	2.2	2.1	1.8	1.9
Powder	0.3	0.4	0.5	0.4	0.5
Other solids	0.4	0.4	0.4	0.3	0.4
Radiation cured	0.05	0.09	0.1	0.09	1.3
Total	7.5	8.2	9.5	7.8	8.8

Source: Kusumgar, Nerlfi, and Growney 2015, U.S. Paint & Coatings Industry, Elmwood Park, NJ.

**TABLE 1.9 U.S. Production of Synthetic Rubber
(Millions of Pounds)**

	2008	2014
Styrene-butadiene	1750	1400
Polybutadiene	1210	900
Nitrile	180	51
Ethylene-propylene	540	960
Other	1100	1700

Source: International Institute of Synthetic Rubber Producers, Houston, TX.

**TABLE 1.10 U.S. Production of Paper and Paperboard
(Million Metric Tons; 2012)**

Type	Amount
Total pulp/paper/paperboard	75.5
Corrugated/packaging	45.9
Newsprint	2.9
Writing/printing	16.1
Others	10.6
Recovered paper	46.4

Source: Paper and Paperboard Recovery, Institute of Scrap Recycling Industries, Washington, DC. June 6, 2013. <http://www.paperonweb.com/USA.htm>.

TABLE 1.11 Polymer Classes: Natural and Synthetic

Polymeric Materials				
Inorganic		Organic/Inorganic	Organic	
Natural	Synthetic		Natural	Synthetic
Clays	Fibrous glass	Siloxanes	Proteins	Polyethylene
Cement	Poly(sulfur nitride)	Polyphosphazenes	Nucleic acids	Polystyrene
Pottery	Poly(boron nitride)	Polyphosphate esters	Lignins	Nylons
Bricks	Silicon carbide	Polysilanes	Polysaccharides	Polyesters
Sands		Sol-gel networks	Melanins	Polyurethanes
Glasses			Polyisoprenes	Poly(methyl methacrylate)
Rocklike				Polytetrafluoroethylene
Agate				Polyurethane
Talc				Poly(vinyl chloride)
Zirconia				Polycarbonate
Mica				Polypropylene
Asbestos				Poly(vinyl alcohol)
Quartz				
Ceramics				
Graphite/diamond				
Silicas				

TABLE 1.12 U.S. Chemical Trade: Imports and Exports (Millions of Dollars)

Business Sector	2004 Exports	2004 Import	2014 Export	2014 Import	2014 Trade Balance
Total chemistry business	105,000	109,000	191,000	197,000	−5,200
Pharmaceuticals	27,000	53,000	52,000	93,000	−42,000
Chemicals excluding pharmaceuticals	78,000	72,000	140,000	103,000	37,000
Agricultural chemicals	4,400	6,300	8,300	12,000	−3,700
Consumer products	5,400	4,600	12,000	9,700	1,900
Basic chemicals	52,000	34,000	92,000	61,000	31,000
Inorganics	6,700	6,300	13,000	9,800	3,100
Bulk petrochemicals and intermediates	24,000	17,000	41,000	32,000	8,500
Plastic resins	16,000	7,700	32,000	14,000	17,000
Synthetic rubber	2,500	1,300	4,400	2,600	1,800
Synthetic fibers	1,900	1,800	2,700	2,500	200
Specialties	17,000	12,000	28,000	20,000	7,400
Coatings	1,600	700	2,900	1,100	1,700
Other specialties	15,000	12,000	25,000	18,000	5,700

Source: Department of Commerce and American Chemistry Council, Washington, DC.

tables, pictures, coaches, curtains, and glass windows; the roads we drive on, the houses we live in, and the buildings we work in; the tapes and CDs we listen to music on; and packaging—all are either totally polymeric or contain a large amount of polymeric materials. Table 1.10 lists some general groupings of important polymers. Welcome to the wonderful world of polymer science.

The number of professional chemists directly employed with polymers as part of their interest and assignment is estimated to be 40%–60% of all the chemists. As the diversity of chemistry increases, the dispersion of those dealing with polymers increases. Polymer chemistry is a major tool applied in biomedical research, synthesis, manufacturing, chemical engineering, pharmaceutical efforts, the environment, communications, etc. “As it was in the beginning,” polymers continue to draw strength from those with diverse training allowing polymers to directly contribute to solutions for most of our technological problems including fuel and transportation, building and construction, communication, and medicine and dentistry. Analytical chemistry is applied to the analysis of materials; inorganic to the catalysts employed in the synthesis of natural and synthetic polymers; organic to the synthesis of diverse materials; physical to describe the kinetics, thermodynamics, and properties of macromolecules; and biological chemistry that deals intently with biopolymers.

Polymeric materials, along with most other chemical industrial products, contribute positively to the balance of trade (Table 1.12). Thus, polymers play a positive role in our balance of trade.

Essentially, all of the industrially advanced countries of the world have major chemical producers. These producers are involved directly and/or indirectly with some form of synthetic polymers. Table 1.13 contains a partial listing of these companies. Chemistry and polymer chemistry are represented in many other applied chemistry areas including pharmaceuticals and biopharmaceuticals. Table 1.14 contains the top 25 pharmaceutical companies according to global sales.

Thus, polymers play a critical role in our everyday lives, actually forming the basis for both plant and animal life, and represent an area where chemists and other scientists and engineers continue to make important contributions.

1.4 ENVIRONMENTAL ASSESSMENT

Daily, we are becoming more aware of the importance of environmental planning and good environmental actions (practices) and their effect on us. This emphasis is being driven by a number of pressures including federal and state laws and initiatives, industrial consciousness, reality,

**TABLE 1.13 Top 50 Global Major Chemical Producers
Based on (Net) Sales (in Millions of
U.S. Dollars; 2014)**

<i>Africa</i>	
South Africa	
Sasol	10,000
<i>Asia</i>	
China	
Sinope	43,000
India	
Reliance Inds.	16,000
Japan	
Mitsubishi Chem	26,000
Sumitomo Chem	18,000
Mitsui Chem	17,000
Toray Inds.	17,000
Shin-Etsu Chem	12,000
Asahi Kasei	11,000
DIC	8,200
Tosoh	7,700
South Korea	
LG Chem	21,000
Lotte Chem	14,000
SK Innovation	12,000
Hanwha Chem	7,700
Thailand	
Siam Cement	7,600
Indorama	7,500
Twain	
Formosa plastics	37,000
PTT Global Chem	10,000
<i>Europe</i>	
Austria	
Borealis	11,000
Belgium	
Solvay	14,000
France	
Air Liquide	19,000
Arkema	7,900
Germany	
BASF	79,000
Bayer	28,000
Linde	19,000
Evonik Inds.	17,000
Lanxess	11,000
The Netherlands	
LyondellBasell Inds.	35,000
Shell	25,000
AkzoNobel	19,000
DSM	12,000
Norway	
Yara	15,000

(Continued)

TABLE 1.13 (Continued) Top 50 Global Major Chemical Producers Based on (Net) Sales (in Millions of U.S. Dollars; 2014)

Switzerland	
Ineos	30,000
Syngenta	11,000
UK	
BP	7,300
Johnson Matthey	7,200
Middle East	
Saudi Arabia	
SABIC	43,000
South America	
Brazil	
Braskem	20,000
United States	
DOW Chemical	58,000
ExxonMobil	38,000
DuPont	30,000
PPG Inds.	14,000
Chevron Phillips Chem	13,000
Praxair	12,000
Huntsman	12,000
Air Products and Chem	10,000
Eastman Chem	10,000
Mosaic	9,100
Ecolab	7,200

Source: C & EN, 92 (30), July 28, 2014.

international efforts, and individual actions. Chemistry, chemists, and the chemical industry have been directing much effort in this direction for over several decades with this effort magnified over the past several years. This textbook highlights some of these efforts in polymers. Here a number of terms will be introduced related to these efforts. While these terms are described individually, the environmental activity is a matrix of actions and activities each one dependent on others to be successful. Many of these studies and assessments are governed somewhat by procedures described by the International Organization for Standardization (ISO). (More about ISO can be found on the web and in Appendix D.)

1.4.1 ENVIRONMENTAL IMPACT ASSESSMENT

An environmental impact assessment (EIA) is simply an assessment of the possible impact that a project or material may have on the natural environment. This possible impact may be positive or negative and often is a combination of positive and negative impacts. The intension of such EIAs is to identify where changes can and should be made and to make us aware of these instances. The International Association for Impact Assessment describes such impact assessments as a process for “identifying, predicting, evaluating, and mitigating the biophysical, social, and other relevant effects of development proposals prior to major decisions being taken and commitments made” (Petts, 1999). The need and specifications for EIAs depend on the particular country. For the United States, it originated as part of the National Environmental Policy Act of 1970. States may also have other requirements.

TABLE 1.14 Top 25 Pharmaceutical Companies Based on Global Sales (in Millions of U.S. Dollars; 2014)

Company	Sales (Millions US\$)
Novartis	47,000
Pfizer	46,000
Roche	39,000
Sanofi	36,000
Merck & Co.	36,000
Johnson & Johnson	32,000
GlaxoSmithKline	30,000
Astra Zeneca	26,000
Gilead Sciences	24,000
Takeda	20,000
AbbVie	20,000
Amgen	19,000
Teva	18,000
Lilly	17,000
Bristol-Myers Squibb	16,000
Bayer	15,000
Novo Nordisk	15,000
Astellas	14,000
Boehringer Ingelheim	14,000
Actavis	13,000
Otsuka	11,000
Daiichi Sankyo	10,000
Biogen Idec	9,400
Baxter	8,800
Merck KGaA	7,700

Source: Global Data in Chemical and Engineering News, Washington, DC.

1.4.2 ECOLOGICAL FOOTPRINT

The ecological footprint is a measure of our demand on the Earth's ecosystems. It includes our demand on both natural resources and on the ability for these resources to be regenerated. In the past, the methods and items to be measured varied widely, often based on factors suiting the particular sector making the footprint assessment. Today, more homogeneous standards are emerging. It is intended to reflect a measure of the land, freshwater, and ocean area required to produce, for instance, a product. Such footprints are often calculated to reflect other average measures. One such measure is a per capita ecological footprint that compares consumption and lifestyles with the natural ability to provide this consumption.

1.4.3 LIFE CYCLE ASSESSMENT

A life cycle assessment (LCA) investigates and evaluates the environmental impact of a product or service. It is also referred to as an ecobalance analysis, cradle-to-grave analysis, and life cycle analysis. Such assessments are intended to measure the effects of the cascade of technologies related to products and services. Here we will restrict our comments to products. "Life cycle" can refer to a holistic assessment of raw material used in the production of a product including energy consumption for procurement and transport of the material, manufacture, distribution, use, and finally disposal (including recycling if possible) environmental costs. Often, guesses and averages are included in these studies. Thus, the cost of transportation

could include some proportion of the truck or train construction, road or rail construction, and the deterioration and repair of same.

According to ISO 14040 and 14044 standards, an LCA contains four distinct phases. These phases are goal and scope, inventory analysis, impact assessment, and interpretation of the first three phases. In the “goal and scope” phase, the functional unit is described with effort focused on defining the boundaries of the system or product to be studied. It includes describing the methods used for assessing possible environmental impacts and which impact categories are to be included in the study. In the “inventory” phase, data are collected including the description and verification of the data along with various modeling programs to be used. Generally, items considered include inputs such as quantities of materials, land usage, and energy and outputs such as air emission, solid waste, and water emissions. Software packages have been developed, and are being developed, to assist in such evaluations. The “impact” phase is intended to describe contributions to more global situations such as global warming and acidification. The final phase, “interpretation,” brings together the other three phases and conclusions are made.

There are varying types of LCA studies that act to limit or define the type of LCA study being made. The *cradle-to-grave* assessment is a full LCA study from manufacture (cradle) to the disposal (grave) of a product. A *cradle-to-gate* study looks at the life cycle from manufacture (cradle) to factory gate (before it is sent to the consumer). These assessments are often used as a basis for environmental product declarations. A *cradle-to-cradle* assessment involves products where the product is recycled so the study terminates when a new product is made from the recycled original product. A *life cycle energy analysis* looks at all energy inputs to a product and not solely direct energy inputs during manufacture including energy necessary to produce components and materials needed for the manufacturing process.

1.5 MANAGING SUSTAINABILITY

Earth, air, fire, and water, not the music group but rather the Greek classical elements, representing the critical elements of global sustainability. Our ability to manage these elements will determine the sustainability of human life as we know it. The need for sustainability is not a recent phenomenon but one on the “front burner.” The most cited definition of sustainability is from the UN World Commission on Environment and Development (Brundtland Commission) that says “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”

Earth represents food, EPA sites, etc.; *air*, our atmosphere and need for breathable air; *water*, the necessity for safe drinking water; and *fire*, our energy. Currently, we are sinking further toward and past the “tipping point” for each of these. A tipping point is generally defined as when some feature reaches a point where various “feedback” loops are not able to compensate for unwanted movement toward (here unwanted) consequences and the movement toward these unwanted consequences becomes more rapid and/or permanent.

The magnitude of the problem or opportunity is great. More than 80 countries and 1 billion people do not have a good source of safe water. About 87 million barrels of nonrenewable crude oil are pumped daily resulting in over 3.5 billion gallons each day with most of this employed as fuel with the remaining used for the production of plastics, drugs, rubbers, paints, fibers, etc.

The polymer industry is part of this challenge and polymers play an essential role in solutions as the materials that allow us to perform the needed tasks to allow us to have safe water and air, efficient use of fuel and an earth that allows us to thrive. Polymers are integral parts of filtering systems for water and air; lighter components for transportation systems and serve as the basis for more fuel efficient engines; polymeric growth hormones and gene engineered seeds can help feed us.

Our reply to issues of sustainability is critical and involves many stakeholders. Managing this reply is critical. The following illustrates some of the inner-relationships and complexity related to the “elements” and their management.

The Florida peninsula receives unwanted mercury from three major sources. The three sources are natural, past agricultural practices, and atmospheric. The atmospheric mercury comes from two main sources. The first is the result of gold retrieval when gold ore is heated with mercury

in open containers in South America allowing mercury to escape into air. The second source is Europe and is connected to ore production and coal burning. The atmospheric mercury finds its way over Florida and is deposited from the sky during violent summer storms. This example illustrates several key factors in addressing sustainability. First, the sources are identified through research highlighting the need for science to contribute to sustainability solutions. Second, there are no governing and enforcement agencies that successfully control such emissions. Third, globalization is a feature since the mercury is moved from country and continent to country and continent. Fourth, the problem is complex and not easily solved. Fifth, environmental problems are often comprised of past and present practices.

Another feature that should be recognized is unintended consequences. One of the initial efforts at producing genetically engineered corn was dropped because the genetically engineered plant killed butterflies that were a chief means of pollinating the corn. For several decades, no new petroleum refining plants have been constructed mainly because of the seemingly excessive cost associated with meeting the “new” environmental regulations.

We will take a moment to describe the situation with respect to biofuels. While ethanol production helps decrease our dependence on “foreign” oil, it is not our answer to energy independence. Ethanol can be made from corn, but this approach suffers from several problems. While corn is a renewable source of ethanol fuel, it is also a source of food; so as corn production for food is diverted to fuel production, the price of corn products increases. Only about a net 20% energy is realized from the production of ethanol from corn when including the energy needed for its production. The production of ethanol is water intensive. Further, calculations show ethanol production from corn is acre limited with only a reasonable 10% of our overall fuel consumption possible through this venue. The problem of supplying ethanol as a fuel is partially solved with the blending of ethanol with regular petroleum-based fuels. The long-range fuel reduction and automotive performance and care have not yet been established.

Research shows some alternatives to the present ethanol production from corn. One alternative is the production of plants that give greater fuel production for acre. Another alternative, and one where the energy tab is low, employs especially designed microbes, mainly bacteria, which convert carbohydrate biomasses into alcohols, mainly ethanol and methanol. These alternatives illustrate other possible solutions. “Total” solutions are often complex with multiple “solutions” needed. Energy solutions must depend on many sources including coal, biofuels, nuclear, direct solar, hydrogeological, and biosolar.

Global warming illustrates the political nature of most sustainability issues. While the press is fully convinced that global warming is a fact and that we are responsible, many scientists are not totally on board with this conclusion. There are abundant scientific studies to support both sides. Even so, with a sustainability issue that can have such dramatic consequence affecting all of humanity, it is better to treat it as real until it is overwhelmingly shown to be false. Thus, there is sufficient scientific information that supports global warming, whether it is a majority or not, as a fact it must be dealt with in a reasonable manner. Note the “reasonable” clause. Today, there are emerging countries, as well as first-world nations, which must act as responsible citizens of earth, but this means that the emerging countries be allowed to “emerge” and the current first-world countries be allowed to exist without great damage to them. This is a balancing act and points out another factor that is important as we address global issues. This factor is to allow some independence of nations while recognizing their interdependence.

All of the major sustainability issues influence our personal health and our business and industrial economies.

We now move toward managing sustainability. The stakeholders are many. Here we will assume the most important stakeholders are you and me. We contribute by influencing legislation, voting, membership in groups, etc. We also contribute through recycling, use of reduced energy consuming transportation, lights, appliances, etc. Sociological and psychological components are also important.

The important stakeholders include

1. Research
2. Business and industry

3. Governmental and legislative including enforcement
4. Environmental and related groups
5. Us

Thus far, all of these stakeholders have shown an inability to effect needed positive change on a global basis. On the research side, while lots of research is being done, it is not globally focused and it has not been shown to appropriately interact with some of the other major stakeholders. Most scientific (including engineering) organizations are small, national, and poorly funded. The largest single discipline organization is the American Chemical Society with 160,000 members, mostly in the United States. It is mainly funded by membership dues and information-related activities. While it attempts to highlight sustainability issues and has a governmental action arm, it lacks sufficient funding and legislative connections. Multidiscipline organizations such as Sigma Xi also suffer from inadequate funding, industrial and business, and legislative governmental connections.

Business and industry is already global and must play a critical role in managing sustainability. They have the multinational ability to influence change on a global way. They lack the primary focus, legislative, and enforcement power as well as “free” funds to assist in the research necessary to understand and influence sustainability.

Governmental and legislative stakeholders have shown an inability to manage sustainability. While some good has come from such entities as the UN and World Bank, they lack the power and funds to adequately manage sustainability. Environmental and related groups are without sufficient funds and research capability. Even so, they are a critical stakeholder often influencing needed legislation that in turn acts as an incentive to obey directives.

Thus, each stakeholder is important and currently all lack some crucial aspect to lead in the management of sustainability.

There is a related question. Are we willing to pay for sustainability and “green” products? Many automobiles that are supposedly green, such as hybrid models, often cost 10%–20% higher than a similar model that burns regular petrol-based fuel. Based on savings on fuel alone, it takes a few years to break even and by then the battery or other “green” energy-producing “motor” parts may need replacing. In studies with bioplastic containers, it appears that consumers are not willing to pay more for their food and drinks coming from biobased containers. In 2010, Stonyfield switched from polystyrene yogurt-derived containers opting to go with “green” poly(lactic acid)-derived yogurt containers that offer a 48% global warming potential savings compared with petrol-based packaging. It was found that consumers, that is, us, were unwilling to pay extra for the container. In 2011, Stonyfield switched from petrobased polyethylene to biobased polyethylene for their smoothie bottles. This switch offered a 65% reduction in warming potential but consumers were not willing to pay extra for the green poly(lactic acid) material. A similar result was observed by Coca-Cola with their bottled water derived from biobased produced ethylene glycol. In order to compete, the price of the biobased polymer was reduced allowing the container price to remain the same. As the cost of biobased materials decreases, this should become less of a problem, but it does raise a question: how much are we willing to pay to be “green?”

Hopefully, this text will allow you both to see where polymers are part of the solution to sustainability and to allow you to become informed in one of the most scientifically important disciplines, polymer science, which will supply many of the materials and knowledge needed to allow a sustainable world.

SUMMARY

After reading this chapter, you should understand the following concepts:

1. Polymers or macromolecules are giant molecules with large structures and high molecular weights. In spite of their varieties, they are governed by the same laws that apply to small molecules.
2. If we disregard metals and some inorganic compounds, practically everything else in this world is polymeric. Polymers form the basis for life itself and for our communications,

transportation, buildings, food, etc. Polymers include protein and nucleic acids in our bodies, the fibers (natural and synthetic) we use for clothing, the protein and starch we eat, the elastomers in our automotive tires, the paint, plastic wall and floor coverings, foam insulation, dishes, furniture, and pipes.

3. There are some systems in place that allow us to readily identify the nature of many polymeric materials including clothing and containers.
4. Early developments in polymers were largely empirical because of a lack of knowledge of polymer science. Advancements in polymers were rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and many other scientists.
5. This is truly the age of the macromolecule. Essentially, every important problem and advance includes polymers including synthetic (such as carbon nanotubes) and biological (such as the human genome and proteins). There are more chemists working with synthetic polymers than in all of the other areas of chemistry combined.
6. The so-called green chemistry is becoming increasingly important in today's chemical industry. The use of naturally derived monomers and polymers is increasing. We are part of the overall solution as informed citizens and scientists.

GLOSSARY

ABS: A polymer produced by the copolymerization of acrylonitrile, butadiene, and styrene.

Bakelite: A polymer produced by the condensation of phenol and formaldehyde.

Cellulose: A naturally occurring carbohydrate polymer.

Ecological footprint: A measure of our demand on the Earth's ecosystems.

Elastomer: A rubber.

Environmental impact assessment, EIA: An assessment of the possible impact that a project or material may have on the natural environment.

Filament: The individual extrudate emerging from the holes in a spinneret; forms fibers.

Functionality: The number of reactive groups.

Intermolecular forces: Secondary forces between macromolecules.

Intramolecular forces: Secondary forces within the same macromolecular chain.

Life cycle assessment, LCA: Investigation and evaluation of the environmental impact of a product or service. It is also referred to as an ecobalance analysis, cradle-to-grave analysis, and life cycle analysis.

Linear: A continuous chain.

Macromolecule: A polymer. Large chained molecular structure.

Natural rubber (NR): Polyisoprene obtained from rubber plants. *Hevea brasiliensis*.

Nylon 66: A polyamide produced from the condensation of adipic acid and 1,6-hexanediamine. Nylon 66 is also given a number of other similar names such as nylon-6,6, nylon-66, and nylon 6,6.

Oligomer: Low-molecular-weight polymer with generally 2–10 repeat units.

Plasticizer: An additive that reduces intermolecular forces in polymers making it more flexible.

Polymer: A giant molecule, macromolecule, made up of multiple repeating units where the backbone is connected by covalent bonds.

Protein: A natural polyamide composed of many amino acid-derived repeat units.

Rayon: Regenerated cellulose in the form of filaments.

Sustainability: Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Thermoplastic: A linear polymer that softens when heated.

Thermoset: A network polymer containing chemical cross-linking that does not soften when heated.

Vital force concept: A hypothesis that stated that organic compounds can be produced only by natural processes and not in the laboratory.

Vulcanization: Process where elastomers such as natural rubber are cross-linked by heating with sulfur.

EXERCISES

1. Name six polymers that you encounter daily.
2. Why are there more chemists that work with polymers than with other areas?
3. Why are there so many outstanding polymer chemists alive today?
4. Which of the following are polymeric or contain polymers as major components?
(a) Water, (b) Wood, (c) Meat, (d) Cotton, (e) Tires, and (f) Paint
5. Name three inorganic polymers.
6. Name three synthetic polymers.
7. Look at the bottom of several containers. Identify what the bottles are made of from the following recycling codes found on their bottoms: (a) 4 with the letters LDPE, (b) 6 with the letters PS, and (c) 5 and the letters PP.
8. Why is there a time delay between discovering a new polymer and commercializing it?
9. What are some advantages of polymers over metals?
10. It has been said that we are lacking exhibitions of the importance of polymers. Explain.
11. Why are polymer-intensive industries often located in the same geographical area?
12. Why might simple identification codes such as those employed for containers fail for objects such as sneakers and tires?
13. How can we become more environmentally responsible?

FURTHER READING

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GENERAL ENCYCLOPEDIAS AND DICTIONARIES

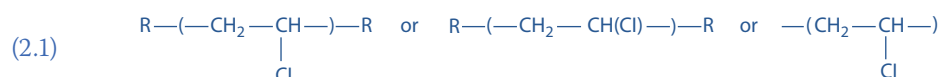
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Polymer Structure (Morphology)

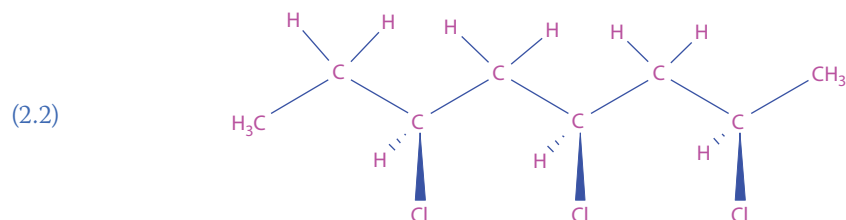
The size and shape of polymers are intimately connected to their properties. The shape of polymers is also intimately connected to the size of the various units that comprise the macromolecule and the various primary and secondary bonding forces that are present within the chain and between chains. This chapter covers the basic components that influence polymer shape or morphology.

We generally describe the structure of both synthetic and natural polymers in terms of four levels of structure. The “**primary structure**” describes the precise sequence of the individual atoms that compose the polymer chain. For polymers where there is only an average structure, such as proteins, polysaccharides, and nucleic acids, a representative chain structure is often given.

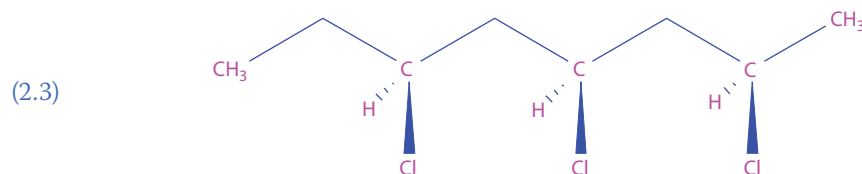
For most synthetic polymers, the structure can be given as a single repeat unit such that the full polymer structure can be obtained by simply repeating the repeat unit 100, 500, or 1000 times depending on the precise number of repeat units in the polymer chain. For poly(vinyl chloride) (PVC), this is



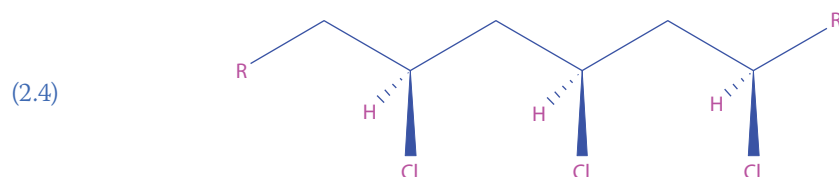
Or some fuller description of the primary structure for PVC may be given such as in the following for three repeat units with methyl end-groups for (2.2) and (2.3) and unspecified end-groups for (2.4) where the particular geometry about each chiral carbon is given:



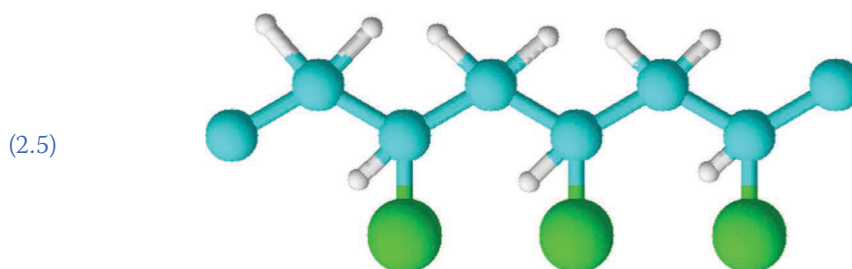
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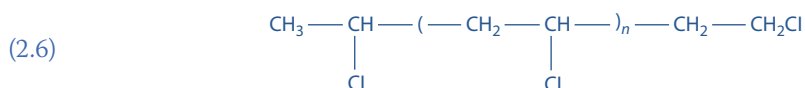
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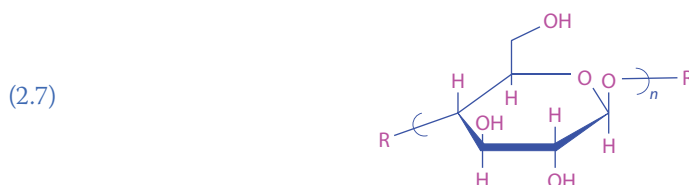
or



The ends may or may not be given depending on whether they are important to the particular point being made. Thus, for the single PVC repeat unit given earlier as in (2.2) and (2.3), the end groups may be given as follows:



In many cases, the simple repeat unit may be given. Thus, the repeat unit for cellulose is



The “secondary structure” describes the molecular shape or conformation of the polymer chain. For most linear polymers, this shape approaches a helical or “pleated skirt” (or sheet) arrangement depending on the nature of the polymer, treatment, and function. Examples of secondary structures appear in Figures 2.9 and 2.13.

The “tertiary structure” describes the shaping or folding of the polymer. Examples of this are given in Figures 2.16b and 2.17a and c.

Finally, the “quaternary structure” represents the overall shape of groups of the tertiary structures where the tertiary structures may be similar or different. Examples are found in Figures 2.15, 2.16a, and 2.17b.

2.1 STEREOCHEMISTRY OF POLYMERS

The terms “memory” and “to remember” are similar and used by polymer chemists in similar, but different ways. The first use of the terms *memory* and *to remember* involves reversible changes in the polymer structure usually associated with stress–strain deformation of a rubber material where the dislodged, moved polymer segments are connected to one another through chemical and physical cross-links so that once the particular stress–strain is removed the polymer returns to its original, prestress–strain arrangement of the particular polymer segments. Thus, the polymer “remembers” its initial segmental arrangement and returns to it through the guiding of the cross-links.

The second use involves nonreversible changes of polymer segments and whole chain movements also brought about through stress–strain actions. These changes include any synthetic chain and segmental orientations as well as postsynthesis changes including fabrication effects. These changes involve “permanent” differences in chain and segmental orientation and in some ways these changes represent the total history of the polymer materials from inception (synthesis) through the moment when a particular property or behavior is measured. These irreversible or nonreversible changes occur with both cross-linked and non-cross-linked materials and are

TABLE 2.1 Typical Properties of Straight-Chain Hydrocarbons

Average Number of Carbon Atoms	Boiling Range (°C)	Name	Physical State at Room Temp.	Typical Uses
1–4	<30	Gas	Gas	Heating
5–10	30–180	Gasoline	Liquid	Automotive fuel
11–12	180–230	Kerosene	Liquid	Jet fuel, heating
13–17	230–300	Light gas oil	Liquid	Diesel fuel, heating
18–25	305–400	Heavy gas oil	Viscous liquid	Heating
26–50	Decomposes	Wax	Waxy	Wax candles
50–1000	Decomposes		Tough waxy to solid	Wax coatings of food containers
1000–5000	Decomposes	Polyethylene	Solid	Bottles, containers, films
>5000	Decomposes	Polyethylene	Solid	Waste bags, ballistic wear, fibers, automotive parts, truck liners

largely responsible for the change in polymer property as the material moves from being synthesized, processed, fabricated, and used in whatever capacity it finds itself. Thus, the polymeric material “remembers” its history with respect to changes and forces that influence chain and segmental chain changes. The ability of polymers to “remember” and have a “memory” is a direct consequence of their size.

We can get an idea of the influence of size in looking at the series of hydrocarbons as the number of carbon atoms increases. For hydrocarbons composed of low numbers of carbons, such as methane, ethane, propane, and butane, the materials are gases at room temperature. For the next grouping such as hexane and octane (Table 2.1), the materials are liquids. The individual hydrocarbon chains are held together by dispersion forces that are a sum of the individual methylene and end group forces. There is a gradual increase in boiling point and total dispersion forces for the individual chains until the materials become waxy solids such as found in bees waxes and birthday candles. Here, the total dispersion forces are sufficient to be greater than individual carbon–carbon bond strengths so the chains decompose prior to their evaporation. These linear chains are sufficiently long to be crystalline waxy solids but not sufficiently long to allow the chains to interconnect various crystalline groupings. Thus, they are brittle solids with little physical strength. As the chains increase in length, the chain lengths are finally sufficient to give tough solids we call linear polyethylene (PE). It is interesting to note that many rocks and diamonds are very strong but brittle because they exhibit essentially no flexibility. Single almost completely linear PE crystals can be grown, which are very strong but brittle. But most linear PE chains gain strength and some flexibility from the chains being sufficiently long to connect the various crystalline domains into larger groupings. This connecting also allows applied forces to be distributed throughout the surrounding areas on a micro-level.

Linear PE generally contains some portions that are not completely regular or crystalline. These regions are referred to as amorphous and introduce into the PE flexibility with sufficient free volume to allow some segmental mobility. Since most linear PE is not completely linear but contains some branching, this branching prevents complete ordering of the chains contributing to the formation of amorphous regions. These amorphous regions include the portions of the chains that interconnect the various ordered regions as well as regions resulting from the branching and other related phenomena. Thus, synthetic PE generally contains both *crystalline* regions where the polymer chains are arranged in ordered lines and which impart strength to the material and they contain *amorphous* regions where the chains are not arranged in ordered lines, and these amorphous regions contribute flexibility with the combination giving a strong material that on the basis of weight can be stronger than steel. The tensile strength/density for bulk steel is 500, while for ultrahigh-molecular-weight polyethylene (UHMPE), it is about 3800. The strength of UHMPE is recognized in many applications including acting as one of the materials employed in the construction of many ballistic resistant body armors (i.e., bulletproof vests), where it acts to both blunt and distribute the energy of incoming projectiles.

As a side note, low-molecular-weight PE with appreciable side branching has a melting range generally below 100°C, whereas high-molecular-weight PE with few branches has a melting range approaching the theoretical value of about 145°C.

In general, most polymers contain some combination of crystalline and amorphous regions providing a material that has a combination of flexibility and strength.

PE chains exhibit irreversible and, when appropriate cross-linking is present, reversible memory because of their size. More about this is discussed in Chapters 8 and 13.

High-density polyethylene (HDPE), formerly called low-pressure PE, $[\text{H}(\text{CH}_2\text{CH}_2)_n\text{H}]$, like other alkanes $[\text{H}(\text{CH}_2)_n\text{H}]$, may be used to illustrate a lot of polymer structure. As in introductory organic chemistry, we can understand the properties and chemical activities of many complex organic compounds if we understand their basic chemistry and geometry. HDPE, like decane $[\text{H}(\text{CH}_2)_8\text{H}]$ or paraffin $[\text{H}(\text{CH}_2)_{\text{about } 50}\text{H}]$, is a largely linear chainlike molecule consisting of catenated carbon atoms bonded covalently. The carbon atoms in all alkanes, including HDPE, are joined at characteristic tetrahedral bond angles of approximately 109.5°. While decane consists of 10-methylene groups, HDPE may contain more than 1000 of these methylene units (Figure 2.1). While we use the term normal or linear to describe nonbranched chains, we know that because of the tetrahedral bond angles and ability for twisting that the chains are zigzag shaped with many possible structural variations.

The distance between the carbon atoms is 1.54 angstroms or 0.154 nanometers (nm). The apparent zigzag distance between carbon atoms in a chain of many carbon atoms is 0.126 nm. Thus, the length of an extended nonane chain is 8 units times 0.126 nm/units = 1.008 nm. For PE, the repeat unit has two methylenes so that the apparent zigzag is 0.252 nm for each “ethylene” unit. The zigzag or contour length of an HDPE chain 1000 units long, $[\text{H}(\text{CH}_2\text{CH}_2)_{1000}\text{H}]$, is 1000 units times 0.252 nm/units or 252 nm. However, because of rotations about the carbon atoms, chains seldom extend to their full extended *contour* length but are present in many different shapes or *conformations*.

The *full contour length* of a polymer is obtained by multiplying the apparent repeat unit length (l), that is, the length of each mer or unit, by the number of units (n); contour length = nl. Even so,

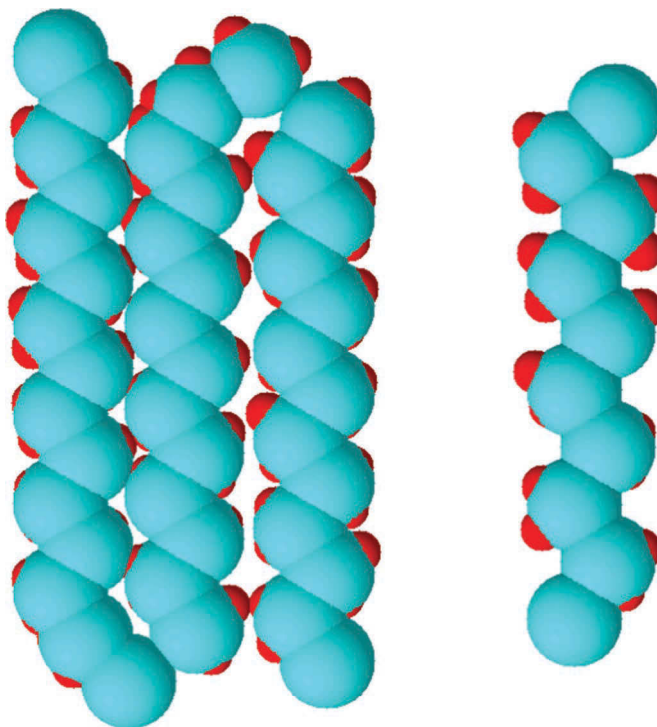


FIGURE 2.1 Simulated structure of high-density polyethylene contrasted with the structural formula of linear or normal decane using space-filling presentation where light blue represents carbon and red hydrogen atoms.

it is important to know the average end-to-end distance of polymer chains. The classical statistical method for this determination, called the random flight technique, was developed by Lord Raleigh in 1919. The classical statistical approach may be used to show the distance traveled by a blindfolded person taking n number of steps of length l in a random walk or the distance flown by a confused moth, bird, or bee.

The distance traveled from start to finish is not the straight-line path measured as nl but the root-mean-square distance $((r^2)^{1/2})$, which is equal to $ln^{1/2}$. Thus, the root-mean-square length of a flexible PE chain with 1000 units is $0.252 \text{ nm} \times (1000)^{1/2} = 7.96 \text{ nm}$ or about 3% of the contour length. Nobel Laureate Paul Flory and others have introduced several corrections so that this random flight technique could be applied to polymer chains approaching a full contour length of nl , that is, rigid rod structures.

Each specific protein molecule has a specific chain length, like classical small molecules, and are said to be monodisperse with respect to chain length or molecular weight. However, most synthetic commercial polymers such as HDPE are composed of molecules of different lengths. Thus, the numerical value for n , or the *degree of polymerization* (DP), should be considered an average DP or average molecular weight. This average notion is often noted by a bar over the top of the DP or M as \bar{M} . Accordingly, the average molecular weight of a *polydisperse* polymer will equal the product of the average DP times the molecular weight of the repeating unit or *mer*.

In organic chemistry, it is customary to call a nonlinear molecule, like isobutane, a branched compound. However, polymer scientists use the term “*pendant group*” to label any group present on the repeat unit. Thus, polypropylene (PP)



has a methyl group as a pendant unit, but PP is designated as a linear polymer. In contrast, low-density polyethylene (LDPE), formally called high-pressure polyethylene, is a branched polymer because chain extensions or branches of methylene units are present coming off of branch points along the typically linear backbone chain (Figure 2.2). For LDPE the frequency of this branching is about 1.5 per 20 methylene units to 1 per 2000 methylene units. This branching, like branching in simple alkanes, increases the specific volume and thus reduces the density of the polymer. The linearity provides strength while the branching provides flexibility and toughness.

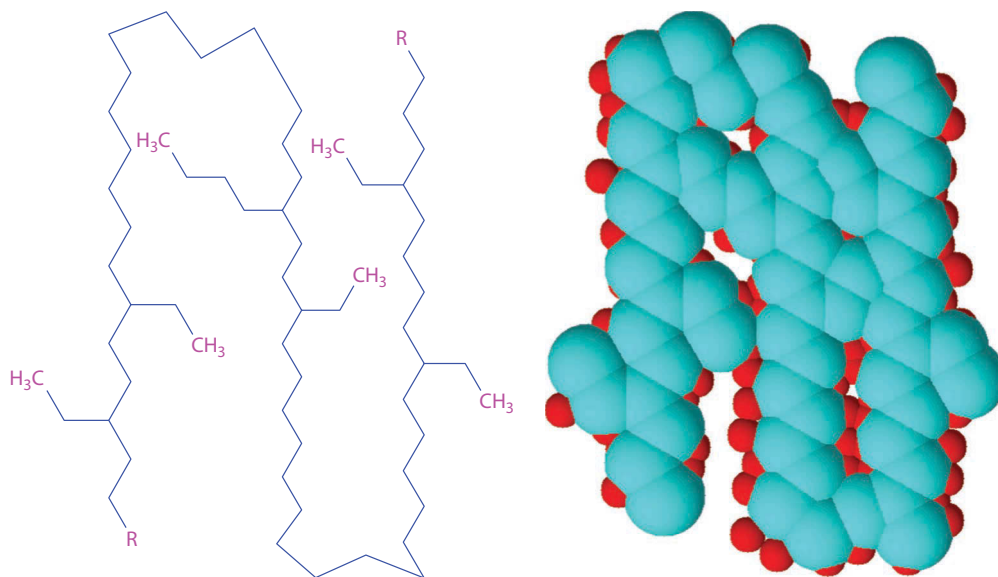


FIGURE 2.2 Simulated structural formula for branched low-density polyethylene; compare with Figure 2.1 for high-density polyethylene using the regular structural depiction, left, and, right, employing a color space-filling representation.

TABLE 2.2 Types of Commercial Polyethylene

	General Structure	Crystallinity (%)	Density (g/cm ³)
LDPE	Linear with branching	50	0.92–0.94
LLDPE	Linear with less branching	50	0.92–0.94
HDPE	Linear with little branching	90	0.95

Recently, low-pressure processes have been developed that produce linear LLDPE that is largely linear but with some branching (Table 2.2).

Both linear and branched polymers are typically “**thermoplastics**” that melt when heated. However, cross-linked 3D, or network, polymers are “**thermoset polymers**” that do not melt when heated but rather decompose prior to melting. The cross-link density can vary from low such as that found in a rubber band to high such as that found in ebonite (Figure 2.3).

While there is only one possible segment arrangement for the repeat unit in HDPE, there are two possible repeat units in PP and many other polymers. The units can be connected using what is called a “**head-to-tail arrangement**” or through a “**head-to-head arrangement**” (Figure 2.4). The usual arrangement by far is the head-to-tail so that pendent methyl groups appear on alternate backbone carbons.

A combination of structure types will be employed in this text. These structure types include simple line drawings such as those given in Figure 2.2; drawings where all of the carbon atoms are given shown in Figure 2.4, left structure; and structures where carbon atoms are added to emphasize particular locations in structures shown in Figure 2.4, right-hand structures. Carbon atoms are also generally given for carbonyl, nitriles, isocyanates, etc., where the location of the carbon

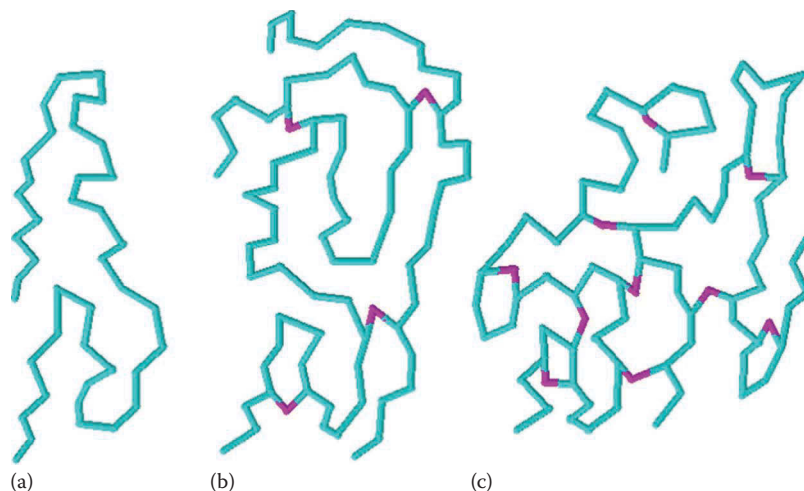


FIGURE 2.3 Skeletal structural formulas of a linear polymer (a) and a network (cross-linked) polymer with low cross-linking density (b) and high-density cross-linking (c). Cross-link sites are noted in magenta.

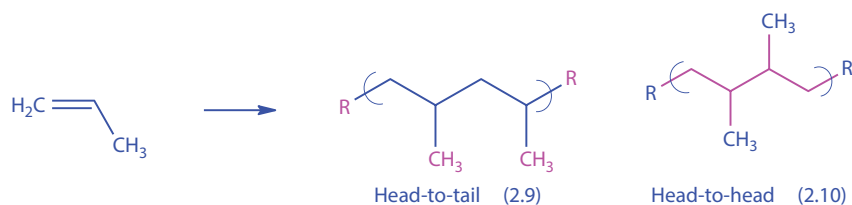


FIGURE 2.4 Simulated structural formulas showing the usual head-to-tail and unusual head-to-head configurations of polypropylene.

atom gives clarity to the particular structure. Often, notations of some carbon atoms will be omitted to emphasize other important structural considerations. Ball-and-stick structures, shown in Figure 2.3, are also utilized. Line drawings are also employed where a simple line represents an unspecified number of units as in Figures 2.14 and 2.15. Space-filling models are also used as shown in Figure 2.16. Thus, structures are given in a number of modes utilized to convey particular structural considerations.

The polymerization of monosubstituted vinyl compounds to give polymers like polystyrene and PP give polymer chains that possess chiral sites on every other carbon in the polymer backbone. Thus, the number of possible arrangements within a polymer chain is staggering since the number of possible isomers is 2^n where “n” is the number of chiral sites. For a relatively short chain containing 50 propylene units, the number of isomers is about 1 times 10^{15} . While the presence of such sites in smaller molecules can be the cause of optical activity, these polymers are not typically optically active since the combined interactions with light are negated by similar, but not identical, other sites contained on the particular and other polymer chains. Further, it is quite possible that no two polymer chains made during a polymerization will be exactly identical because of chiral differences.

The particular combinations of like and mirror image units within a polymer chain influences the polymer properties on a molecular level. On the bulk level, the average individual chain structure influences properties.

In the early 1950s Nobel Laureate Giulio Natta used stereospecific coordination catalysts to produce stereospecific isomers of PP. Natta used the term tacticity to describe the different possible structures. As shown in Figure 2.5, the isomer corresponding to the arrangement DDDDDD or LLLLLL is called “*isotactic*” (same). The isomer corresponding to the DLDLDDL structural arrangement about carbon is called “*syndiotactic*” (alternating). The isomer arrangement that corresponds to some mix of stereo arrangements about the chiral carbons is called “*atactic*” (having nothing to do with). The differences in stereoregularity about the chiral carbon influence the physical properties of the polymers. Thus, those with isotactic or syndiotactic arrangements are more apt to form compact crystalline arrangements and those with atactic stereoregularity are more apt to form amorphous arrangements. Isotactic PP (iPP) has a melting point (MP) of about 160°C and it is highly crystalline, whereas atactic PP (aPP) melts at about 75°C and is amorphous. The term “eutectic” is used to describe either an isotactic or syndiotactic polymer or a mixture of both.

While most polymers contain only one chiral or asymmetrical center in each repeat unit, it is possible to have diisotacticity where two different substituents are present at chiral centers. These isomers are labeled erythro- and threodiisotactic and erythro- and threosyndiotactic isomers (Figure 2.6).

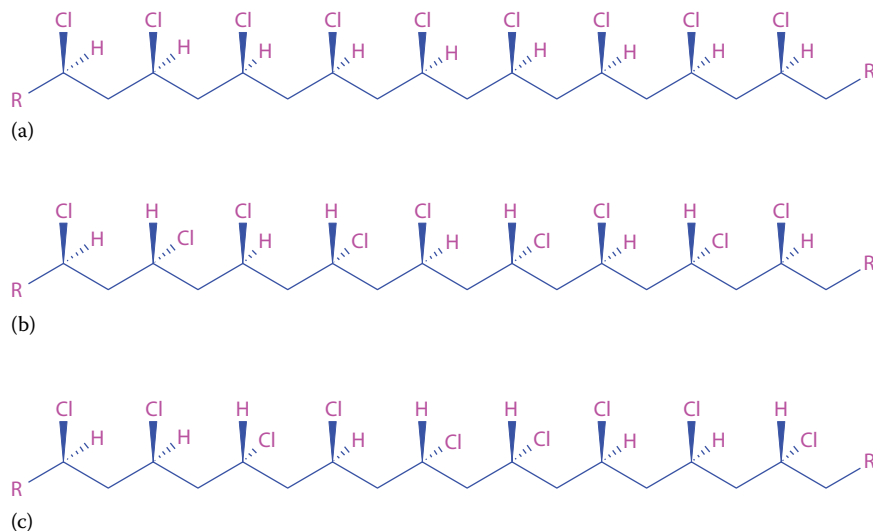


FIGURE 2.5 Skeletal formulas of (a) isotactic, (b) syndiotactic, and (c) atactic of poly(vinyl chloride), PVC.

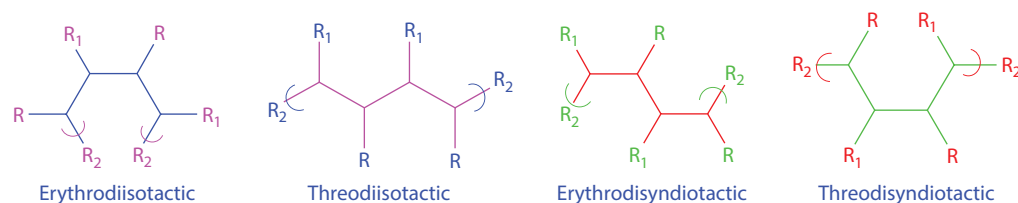


FIGURE 2.6 Simulated formulas of ditactic isomers where R_2 are chain extensions and R and R_1 are not hydrogen.

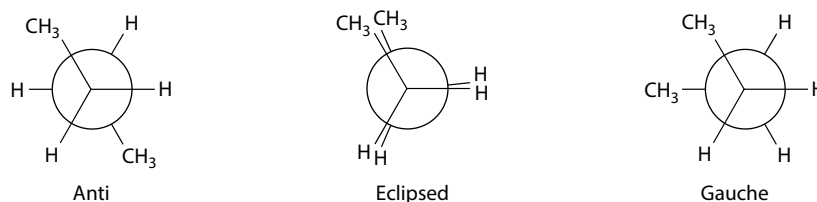


FIGURE 2.7 Newman projections of designated conformers of n -butane.

The many different conformers resulting from rotation about the carbon–carbon bonds in a simple molecule like n -butane may be shown by Newman projections (Figure 2.7). The most stable is the anti or trans projection where the steric hindrance is minimized. There are a number of eclipsed and gauche arrangements of which only one of each is shown in Figure 2.7. The energy difference between the anti and eclipsed, the least stable form, is about 12 kJ/mol.

The ease in going from one conformer to the other conformer decreases as the pendent groups increase in size and secondary bonding. Thus, poly(methyl methacrylate) is hard at room temperature because of the polar groups and steric hindrance. By comparison, polyisobutylene, offering a smaller amount of steric hindrance, is flexible at room temperature.

2.2 MOLECULAR INTERACTIONS

Forces in nature are often divided into primary forces (typically greater than 200 kJ/mol) and secondary forces (typically less than 40 kJ/mol). “**Primary bonding**” forces can further be subdivided into ionic (characterized by a lack of directional bonding, occurs between atoms of large differences in electronegativity, normally not found in polymer backbones), metallic (the number of outer, valence electrons is too small to provide complete outer shells; often considered as charged atoms surrounded by a potentially fluid sea of electrons; lack of bonding direction), and covalent (including dative and coordinate) bonding (the major bonding in organic compounds and polymers, directional). The bonding length of primary bonds is generally about 0.1–0.22 nm. The carbon–carbon bond length is about 0.15–0.16 nm. Atoms in individual polymer chains are joined to one another by covalent bonds with bonding energies about 320–370 kJ/mol.

Polymer molecules are also attracted to one another through secondary forces. Secondary forces, often called “**van der Waals forces**” because they are the forces responsible for the van der Waals corrections to the ideal gas relationships, are of longer distance in interaction, in comparison to primary forces and of less energy. Secondary bonding distances are generally on the order of 0.25–0.5 nm. The force of these interactions is inversely proportional to some power of the distance, generally 2 or greater (i.e., force is proportional to $1/(\text{distance})^n$). Thus, many physical properties are sensitive to the polymer **conformation** (arrangements related to rotation about single bonds) and **configuration** (arrangements related to the actual chemical bonding about a given atom), since both affect the proximity one chain can have relative to another. Thus, amorphous PP is more flexible than crystalline (generally isotactic or syndiotactic) PP because the crystalline PP has the units closer to one another allowing the secondary bonding to be stronger (Figure 2.8).

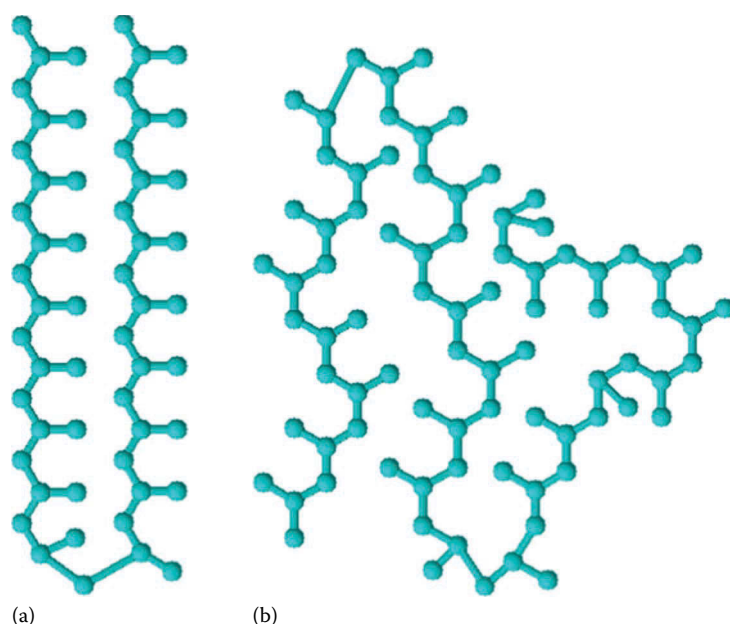


FIGURE 2.8 Representation of a crystalline portion from isotactic polypropylene (a) and an amorphous portion from atactic polypropylene, right using ball, and stick models (b).

These intermolecular forces are also responsible for the increase in boiling points within a homologous series such as the alkanes, for the higher-than-expected boiling points of polar molecules such as alkyl chlorides, and for the abnormally high boiling points of water, alcohols, amines, and amides. While the forces responsible for these increases in boiling points are all van der Waals forces, the forces can be further subdivided in accordance to their source and intensity.

Secondary forces are often divided into four groups. These are shown in Table 2.3. The strongest of these are the *ion-dipole* forces illustrated by the dissolving of common table salt, NaCl, in water. Water possesses a strong dipole and NaCl (actually when dissolved existing as Na^+ and Cl^-) represents ionic compounds. It is often said that salt dissolves in water because the dipole nature of water is sufficient to overcome the ionic forces holding the salt atoms together. In truth, when considering dissolving and mixing, the major driving factor is that mixing and dissolving allow an increase in disorder or increase in entropy. The next chapter deals in greater depth with the phenomenon of dissolving of polymers.

The next strongest group of secondary forces is the dipole–dipole force. Polar molecules such as ethyl chloride and PVC are attracted to each other by both the London forces (described in the following text), but also *dipole–dipole interactions* resulting from the electrostatic attraction of a chlorine atom in one molecule to a hydrogen atom in another molecule. These dipole–dipole forces are of the order of 8–25 kJ/mol, generally greater than the London forces and they are temperature dependent. Hard plastics, such as PVC, have dipole–dipole attractive forces present between the chains.

Probably, the most important of the dipole–dipole interactions is referred to as “*hydrogen bonding*.” Strongly polar molecules such as ethanol, poly(vinyl alcohol), cellulose, and proteins

TABLE 2.3 General Classes of Secondary Forces

Type	Relative Strength
Ion-dipole	Strongest
Dipole–dipole	
Dipole-induced dipole	
Induced dipole-induced dipole	Weakest

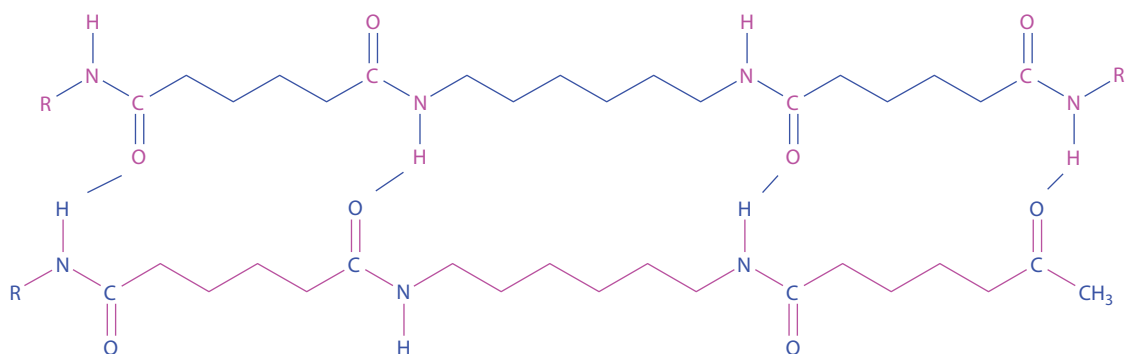


FIGURE 2.9 Typical hydrogen-bonding (shown as “–” between hydrogen on nitrogen and oxygen for nylon 66).

are attracted to each other by this special type of dipole–dipole force. Hydrogen bonding occurs when a hydrogen atom that is bonded to a highly electronegative element, such as nitrogen or oxygen, comes close to another highly electronegative element. These forces are on the order of 40 kJ/mol, and for something like hydrogen fluoride, they are almost as strong as primary bonding. Intermolecular hydrogen bonding is usually present in classical fibers such as cotton, wool, and silk and synthetic polymers such as nylon (Figure 2.9), polyacrylonitrile, polyesters, and polyurethanes. Intramolecular hydrogen bonds are responsible for the helices observed in starch and globular proteins.

The next strongest secondary force group is the “**dipole-induced dipole**.” This group is illustrated by the distortion of nonpolar oxygen molecules by polar water molecules allowing for the presence of sufficient oxygen to allow fish and plants to survive under water. But it is not sufficient to provide enough oxygen to support humans and mammals in water without them rising to the surface periodically to obtain enough oxygen to survive.

The weakest of the secondary forces is the “**induced dipole-induced dipole**” force. All molecules including nonpolar molecules, such as heptane and PE, are attracted to each other by these induced-dipole induced-dipole forces also called “**London**” or “**dispersion forces**.” The temporary or transient dipoles are due to instantaneous fluctuations in the electron cloud density. The energy range of these forces is fairly constant and about 8 kJ/mol. This force is independent of temperature and is the major force between chains in largely nonpolar polymers such as those in classical elastomers and soft plastics such as PE.

It is of interest to note that methane, ethane, and ethylene are all gases; hexane, octane, and nonane are all liquids (at room conditions), while low-molecular-weight PE is a waxy solid. This trend is primarily due to an increase in the mass per molecule and to an increase in the London forces per polymer chain. The London force interaction between methylene units is about 8 kJ/mol. Thus, for methane molecules the attractive force is about 8 kJ/mol, for octane it is about 64 kJ/mol, and for PE with 1000 ethylene (or 2000 methylenes), it is about 2,000 methylene units \times 8 kJ/mol per methylene unit = 16,000 kJ/mol well sufficient to make PE a solid and to break backbone bonds before it boils. (Polymers do not boil because the energy necessary to make a chain volatile is greater than the primary backbone bond energy.)

It is important to note that the high melting point of nylon 66 (Figure 2.9; 265°C) is a result of a combination of dipole–dipole, London, and hydrogen bonding forces. The amount of hydrogen bonding decreases as the number of methylene groups increases such as for nylon-610 and a corresponding decrease is seen in the melting point (215°C). In contrast, iPP, which has no hydrogen bonding holding the PP chains together, is also a strong fiber because of the ability of the similar chains to fit closely together. Thus, both secondary bonding between chains and the ability to tightly fit together, steric and symmetry factors, are important factors in determining polymer properties.

In addition to the contribution of intermolecular forces, chain entanglement is also an important contributory factor to the physical properties of polymers. While paraffin wax and HDPE

TABLE 2.4 Critical Chain Lengths for Some Common Polymers

Polymer	Critical Chain Length (Number of Repeat Units)
Polycarbonate	20
1,4-Polybutadiene	110
Poly(decamethylene adipate)	11
Polydimethylsiloxane	450
Polyethylene	150
Poly(ethylene oxide)	100
Poly(methyl methacrylate)	160
Polypropylene	170
Poly(propylene oxide)	100
Polystyrene	300
Poly(vinyl acetate)	250
Poly(vinyl alcohol)	170
Poly(vinyl chloride)	175

Source: Modified from Sperling, L.H., *Introduction to Physical Polymer Science*, 4th edn., 2005, Wiley, Hoboken, NJ.

are homologs, the chain length of paraffin is too short to permit chain entanglement and hence it lacks the strength and many other physical characteristic properties of HDPE.

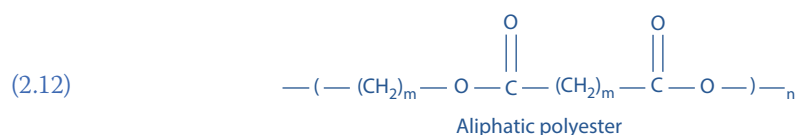
Chain entanglement allows long chains to act as though they were even longer because entanglement causes the entangled chains to act together. Many of the physical properties, such as tensile strength and melt viscosity, of polymers increase dramatically when chain entanglement occurs. The *critical chain length* (z) required for the onset of entanglement is dependent on the polarity and shape of the polymer. Table 2.4 contains experimental critical chain lengths for a number of common polymers.

It is of interest that the critical chain lengths for poly(decamethylene sebacate) and polycarbonate are low in comparison to the other polymers. This is largely a result of the additional interchain forces of attraction, namely, dipolar–dipolar interchain bonding that are present for these two polymers. Thus, the ideal of chain entanglement is important where the interchain forces are not large, such as for many vinyl polymers, but is less important for condensation where the interchain forces are stronger.

“*Viscosity*” is a measure of the resistance to flow. Flow is a result of cooperative movement of the polymer segments from vacate locations, holes, to another vacate location in a melted state. This movement is impeded by chain entanglement, high intermolecular forces, the presence of reinforcing agents, and cross-links. The “*melt viscosity* (η)” is often found to be proportional to the 3.4 power of the critical chain length, as shown in Equation 2.11, regardless of the polymer. The constant K is temperature dependent.

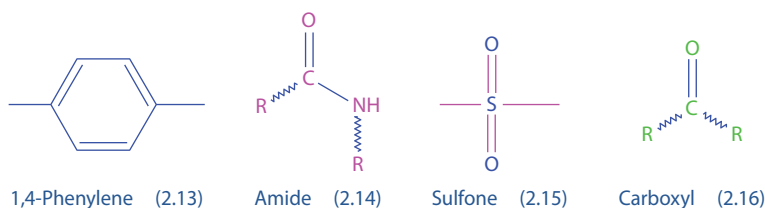
$$(2.11) \quad \log \eta = 3.4 \log z + \log K$$

The flexibility of amorphous polymers above the glassy state is governed by the same forces as melt viscosity and is dependent on a wriggling type of segment motion in the polymer chains. This flexibility is increased when many methylene groups ($-\text{CH}_2-$) or oxygen atoms ($-\text{O}-$) are present. Thus, the flexibility of aliphatic polyesters usually increases as “ m ” is increased (2.12).

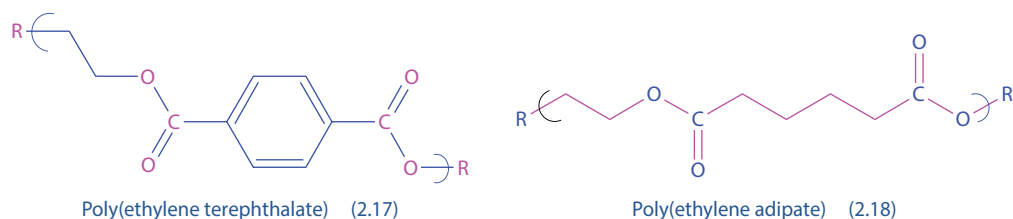


Flexibilizing groups include methylene, ethylene oxides, and dimethylsiloxanes groups.

In contrast, the flexibility of amorphous polymer above the glass state is decreased when stiffening groups such as shown in (2.14) through (2.16)



are present in the polymer backbone. Thus, poly(ethylene terephthalate) (PET; 2.17) is stiffer and higher melting than poly(ethylene adipate) (2.18), and the former is stiffer than poly(butylene terephthalate) because of the presence of fewer methylene groups between the stiffening groups.



2.2.1 GLASS TRANSITION AND MELT TRANSITION

Small molecules such as water can exist in three phases—solid, liquid, and gas. Polymers do not boil so this phase is missing for polymers so they do not exist in the gaseous state. But polymers undergo other transitions besides melting. The most important of these is called the “glass transition,” T_g , which will be discussed in the following text. Before we turn to the glass transition, it is important to note that polymers may undergo many other transitions. About 20 transitions have been reported for PE. Polystyrene undergoes several transitions that have been identified. About -230°C , the movement, often described as wagging or oscillation, of the phenyl groups begins. At about -140°C , movement of four-carbon groups in the polystyrene backbone begins. By 50°C , torsional vibration of the phenyl groups begins. At about 100°C , long-range chain movement begins corresponding to the reported T_g value for polystyrene (Table 2.5). It is important to remember that while small molecules have a precise temperature associated with its transitions,

TABLE 2.5 Approximate Glass Transition Temperatures (T_g) for Selected Polymers

Polymer	T_g (K)	Polymer	T_g (K)
Cellulose acetate butyrate	323	Cellulose triacetate	430
Polyethylene (LDPE)	148	Polytetrafluoroethylene	160,400 ^a
a-Polypropylene	253	Poly(ethyl acrylate)	249
i-Polypropylene	373	Poly(methyl acrylate)	279
Polyacrylonitrile	378	a-Poly(butyl methacrylate)	339
Poly(vinyl acetate)	301	a-Poly(methyl acrylate)	378
Poly(vinyl alcohol)	358	Poly(vinyl chloride)	354
cis-Poly-1,3-butadiene	165	Nylon 66	330
trans-Poly-1,3-butadiene	255	Poly(ethylene adipate)	223
Polydimethylsiloxane	150	Poly(ethylene terephthalate)	342
Polystyrene	373		

^a Two major transitions observed.

such as 0°C for melting for water, polymer values, while often reported as a specific value, are in reality a temperature range. This temperature range is the result of at least two features. First, there is a variety of polymer chain environments at the molecular level each with its own energy-associated features. Second, transitions that require large segment or whole chain movement will also have a kinetic factor associated with them because it takes time for chains to untangle/tangle and rearrange themselves. Thus heating/cooling rate affects the temperatures required to effect the changes.

Polymers generally undergo several major thermal transitions. At low temperatures, most polymers are brittle and glassy since there is not sufficient energy present to encourage even local or segmental chain movement. As the temperature is increased, at some temperature there is sufficient energy available to allow some chain mobility. For a polymer containing both amorphous and crystalline portions or is only amorphous, the onset of this segmental chain mobility for the amorphous segments is called the “glass transition temperature,” T_g . Because there is unoccupied volume in the amorphous polymer structure, some segmental chain movement occurs. This segmental chain movement is sometimes likened to a snake or worm slithering “in place” within the grass. The T_g is then the temperature when the snake or worm begins to wiggle. The localized chain movement causes a further increase in unoccupied volume and larger segments are able to move eventually allowing the snake further movement in the grass. As the temperature is increased, there is sufficient temperature to overcome the forces present in the crystalline portion of the polymer allowing a breaking up of the crystalline portion. This temperature is often referred to as the “crystalline transition temperature,” T_c . This temperature is generally directly related to the “melt transition temperature,” T_m or melting point. Finally, as the temperature continues to rise, there is sufficient energy available to overcome the primary bonds holding the polymer together and the polymer decomposes at the “decomposition temperature,” T_d . The T_g and T_m are described further later.

The flexibility of amorphous polymers is reduced drastically when they are cooled below the “glass transition temperature” (T_g). At temperatures below T_g , there is no ready segmental motion and any dimensional changes in the polymer chain are mainly the result of temporary distortions of the primary covalent bonds. Below the T_g , the chains are “frozen” into place and the material acts as a brittle solid or glass, hence the name “glassy state.” Amorphous plastics perform best below T_g but elastomers must be used above the brittle point, T_g , or they will act as a glass and be brittle and break when bent. The importance of a material being above its T_g to offer some flexibility was demonstrated by the space shuttle Challenger disaster where the cool temperature at the launch pad resulted in the “O” ring not being flexible so that fuel escaped resulting in the subsequent explosion.

The major reasons why amorphous polymers go from a solid glassy state to a more flexible plastic state are the presence of sufficient energy and unoccupied volume. The energy is supplied by heating the sample allowing the polymer sufficient energy for chain segments to become separated and begin movement, which in turn creates free or unoccupied volume that allows the chain segments to slip past one another resulting in the material being more flexible. In order for the chains to begin moving, the secondary forces that hold the chains together must be overcome. As movement begins additional unoccupied volume is created, and this expansion within a complex maze of intertwining chains creates additional free volume. A measure of this expansion is the “thermal coefficient of expansion.” The temperature range where the available free volume and energy necessary to overcome segmental chain interactions is available is called the “glass transition temperature,” T_g . Since the specific volume of polymers increases at T_g in order to accommodate the increased segmental chain motion, T_g values can be estimated from plots of the change in specific volume with temperature (Figure 2.10).

The T_g for isotactic PP is 373 K or 100°C yet, because of its high degree of crystallinity, it does not flow to any great extent below its melting point of 438 K (165°C). In contrast, highly amorphous polyisobutylene, which has a T_g value of 203 K (−70°C), flows at room temperature (Table 2.5). T_g decreases as the size of the ester groups increases in polyacrylates and polymethylacrylates. The effect of the phenylene stiffening groups is demonstrated with the T_g of PET (2.17) being about 120° higher than that of poly(ethylene adipate) (2.18).

The “melting point” (also called the melt transition temperature) is the temperature range where total or whole polymer chain mobility occurs. The melting point (T_m) is called a first-order

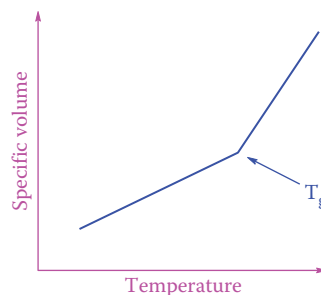


FIGURE 2.10 Determination of T_g by noting the abrupt change in specific volume.

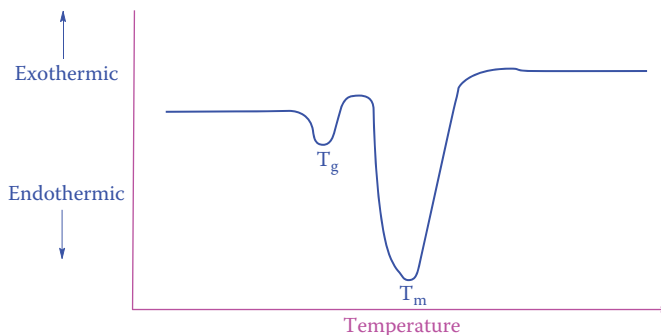


FIGURE 2.11 Typical DSC thermogram of a polymer.

transition temperature, and T_g is sometimes referred to as a second-order transition. The values for T_m are usually 33%–100% greater based on the absolute temperature scale than the T_g . Symmetrical polymers like HDPE exhibit the greatest difference between T_m and T_g . The T_g values are low for elastomers and flexible polymers such as PE and dimethylsiloxane, and relatively high for hard amorphous plastics such as polyacrylonitrile and PET (Table 2.5).

Other properties such as stiffness (modulus), refractive index, dielectric properties, gas permeability, x-ray adsorption, and heat capacity (Figure 2.11) all change at T_g and have been used to determine the T_g . As seen in Figure 2.11, both T_g and T_m are endothermic because energy is absorbed when segmental mobility or melting occurs. Also, causing wholesale mobility takes more energy than causing segmental mobility so that the area under the curve, a direct measure of the heat being taken on to effect the mobility, for the T_m is greater than for T_g where the amount of amorphous and crystalline regions are nearly equal. While T_g values are most often reported related to the onset of segmental motion in the principal polymer backbone, other secondary values may be observed for the onset of motion of large pendant groups, branches, etc.

2.2.2 SECONDARY STRUCTURES

The number of possible conformers increases with chain length and can be shown statistically to equal 2^{2n} where n is the number of units. Thus, when $n = 1000$, the number of possible conformers of HDPE is 2^{2000} or 10^{600} , more than the grains of sand at all of our beaches and even far greater than Avogadro's number. Four of these possible conformers are shown in Figure 2.12.

However, because there are so many possible ends in branched polymers, it is customary to use the radius of gyration (S) instead of end-to-end distance for such polymers. The radius of gyration is actually the root-mean-square distance of a chain end from the polymer's center of gravity. S is less than the end-to-end distance (r), and for linear polymers $r^2 = 6S^2$.

In general, polymers (both natural and synthetic) “emphasize” two general shapes—helical and pleated (Figures 2.9 and 2.13). The intermolecular bonds in many polyamides, including natural polyamides such as β -keratin, produce strong pleated sheets. Hair, fingernails and toenails, feather, and horns have a β -keratin structure. Helical structures are often formed because

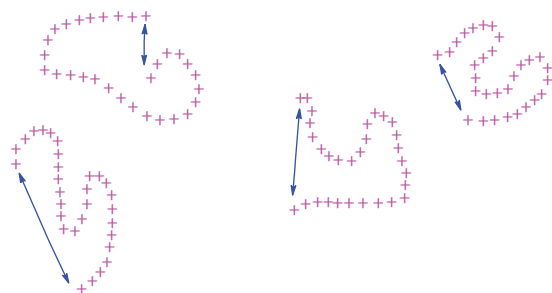


FIGURE 2.12 End-to-end distances for four 30-unit chains.

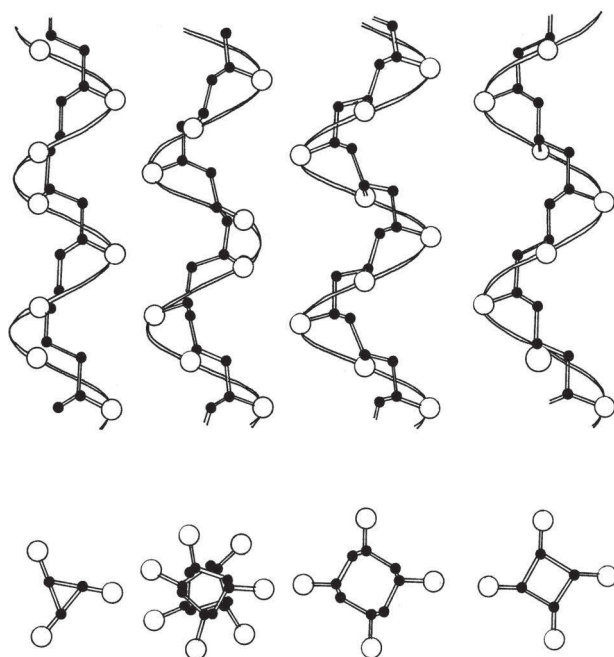


FIGURE 2.13 Helical conformation of isotactic vinyl polymers. (From Gaylord, N., in: *Linear and Stereoregular Addition Polymers*, N. Gaylord and H. Mark, eds., Wiley, NY, 1959.)

they can minimize steric factors by “radiating” bulky groups outward from a core distributing the steric groups about a helical circle. α -Keratin (composed of parallel polypeptide α -helices) and most globular proteins are characterized by intramolecular bonds. These, and many other polymers, including nucleic acids, may form helices. Ribonucleic acid (RNA) exists as a single-stranded helix, while deoxyribonucleic acid (DNA) exists as a double-stranded helix.

2.3 POLYMER CRYSTALS

Prior to 1920, not only leading scientists stated that macromolecules were nonexistent, but they also believed, if they did exist, they could not exist as crystals. However, in the early 1920s, Haworth used x-ray diffraction techniques to show that elongated cellulose was a crystalline polymer consisting of repeat units of cellobiose. In 1925, Katz in jest placed a stretched natural rubber band in an x-ray spectrometer and to his surprise observed an interference pattern typical of a crystalline substance. This phenomenon may be shown qualitatively by the development of opacity when a rubber band is stretched (try it yourself) and by the abnormal stiffening and whitening of unvulcanized rubber when it is stored for several days at 0°C. The opacity noted in stretched rubber and cold rubber is the result of the formation of crystallites, or regions

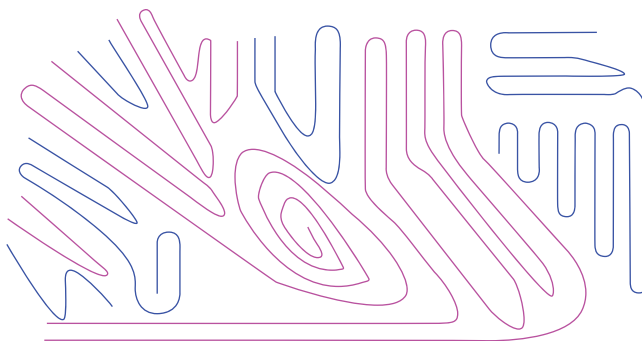


FIGURE 2.14 Schematic 2D representation of a modified micelle model of the crystalline-amorphous structure of polymers.

of crystallinity. The latter were first explained by a fringed micelle model that is now found not consistent with much of the current experimental findings (Figure 2.14).

Amorphous polymers with irregular bulky groups are seldom crystallizable, and unless special techniques are used, even ordered polymers are seldom 100% crystalline. The combination of amorphous and crystalline structures varies with the structure of the polymer and the precise conditions that have been imposed on the material. For instance, rapid cooling of an amorphous polymer sample often decreases the amount of crystallinity because there is not sufficient time to allow the long chains to organize themselves into more ordered structures before they become frozen in place. The reason linear ordered polymers fail to be almost totally crystalline is largely kinetic, resulting from an inability of the long chains to totally disentangle and perfectly align themselves during the time the polymer chain is cooling and mobile.

Mixtures of amorphous and mini-crystalline structures or regions may consist of somewhat random chains containing some chains that are parallel to one another forming short-range mini-crystalline regions. Crystalline regions may be formed from large range ordered platelet-like structures, including polymer single crystals, or they may form even larger organizations such as *spherulites* as shown in Figures 2.15 and 2.16. Short- and longer-range ordered structures can act as physical cross-links.

In general, linear polymers form a variety of single crystals when crystallized from dilute solutions. For instance, highly linear PE can form diamond-shaped single crystals with a thickness on the order of 11–14 nm when crystallized from dilute solution. The surface consists of “hairpin-turned” methylene units as pictured in Figures 2.15 and 2.16. The polymer chain axes are perpendicular to the large flat crystal faces. A single polymer chain with 1000 ethylene (2000 methylene) units might undergo on the order of 50 of these hairpin turns on the top surface and another 50 turns on the bottom face with about 20 ethylene units between the two surfaces.

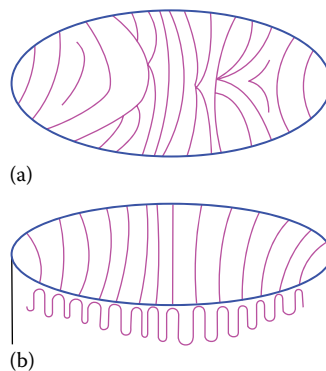


FIGURE 2.15 Structure of a spherulite from the bulk. (b) A slice of a simple spherulite. As further growth occurs, filling in, branch points, etc., occur as shown in the figure (a). The contour lines are simply the hairpin turning points for the folded chains.

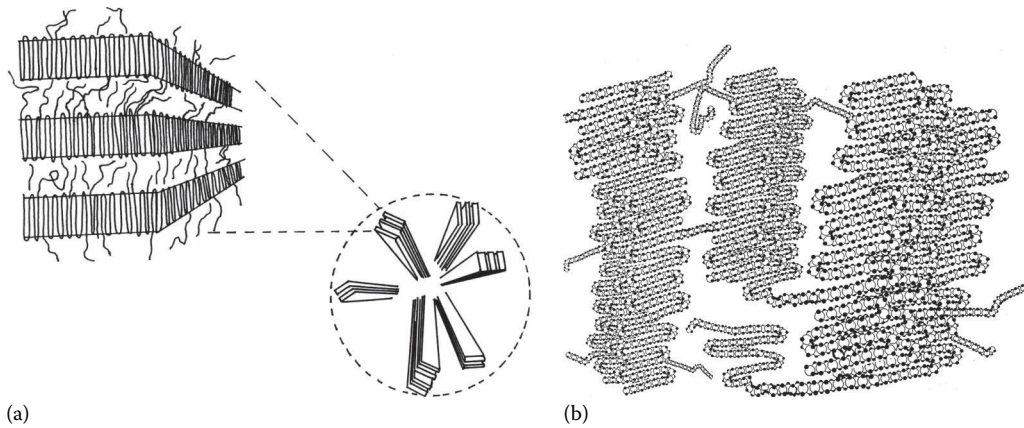


FIGURE 2.16 Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements (a) and a more complete model of two sets of three lamellar chain-folded platelets formed from polyethylene (b). Each platelet contains about 850 ethylene units as shown here.

Many polymers form more complex single crystals when crystallized from dilute solution including hollow pyramids that often collapse on drying. As the polymer concentration increases, other structures occur, including twins, spirals, and multilayer dendritic structures with the main structure being spherulites.

When polymer solids are produced from their melts, the most common structures are these spherulites that can be seen by the naked eye and viewed as Maltese cross-like structures with polarized light and crossed Nicol prisms under a microscope.

For linear PE, the initial structure formed is a single crystal with folded chain *lamellae*. These quickly lead to the formation of sheaflike structures called axialites or hedrites. As growth proceeds, the lamellae develop on either side of a central reference point. The lamellae continue to fan out, occupying increasing volume sections through the formation of additional lamellae at appropriate branch points. The result is the formation of spherulites as pictured in Figures 2.15 and 2.16.

While the lamellar structures present in spherulites are similar to those present in polymer single crystals, the folding of chains in spherulites is less organized. Further, the structures that exist between these lamellar structures are generally occupied by amorphous structures including atactic chain segments, low-molecular-weight chains, and impurities.

The individual spherulite lamellae are bound together by “tie” molecules that are present in more than one spherulite. Sometimes these tie segments form intercrystalline links, which are threadlike structures, which are important in developing the characteristic good toughness found in semicrystalline polymers. They act to tie together the entire assembly of spherulites into a more or less coherent “package.”

Depending upon the particular conditions of crystallization, a number of secondary and tertiary structures can be formed. In most cases, crystalline polymers attempt to form crystalline platelets. Under little or no externally applied stress, these platelets organize themselves in spherulites as pictured in Figures 2.15 and 2.16. They start by a nucleating process and begin to radiate outward from the central nucleating site. Amorphous chain segments get trapped between the forming crystalline platelet combinations giving a kind of a fuzzy or frayed exterior. Either these platelets are generally planar, as shown in Figure 2.17, or they can be helical or twisted. The platelets continue to grow until they butt up against other spherulites.

Under externally applied stress, including simple melt flow, the tertiary structure can approach a shish kebab arrangement where there are planes of platelets separated by areas where there exist both crystalline and amorphous regions as pictured in Figure 2.17, left. These shish kebab structures often organize into quaternary structures consisting of bundles of shish kebab single-strand filaments forming fibrils. Under more rapid flow conditions, the shish kebab itself becomes distorted (Figure 2.17, right).

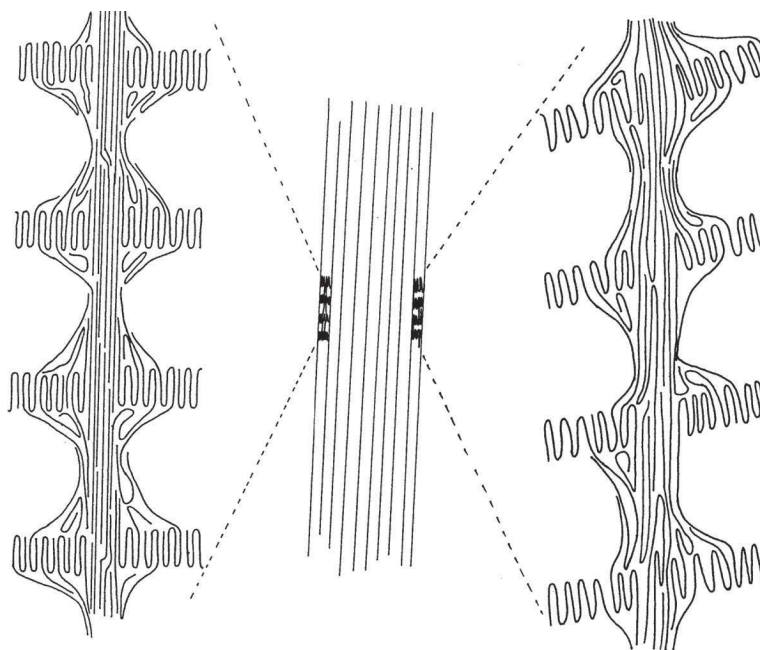


FIGURE 2.17 Crystalline polymer structures formed under applied tension including flow conditions. Middle shows the tertiary mono-fibrillar structure including platelets and at the left shows these mono-fibrillar structures bundled together forming a quaternary structure fibril. Right shows the distorted shish kebab formed with more rapid flow.

Interestingly, the amorphous regions within the spherulite confer onto the material some flexibility while the crystalline platelets give the material strength, just as in the case with largely amorphous materials. This theme of amorphous flexibility and crystalline strength (and brittleness) is a central idea in polymer structure–property relationships.

It must be remembered that the secondary structure of both the amorphous and crystalline regions typically tends toward a helical arrangement of the backbone for most polymers but not PE that forms a crank-shaft structure because of the lack of steric restraints (i.e., lack of pendent groups off the backbone).

The kind, amount, and distribution of polymer chain order/disorder (crystalline/amorphous) is driven by the processing (including pre- and post-) conditions and thus it is possible to vary the polymer properties through a knowledge of and ability to control the molecular-level structures. The crystalline regions may be disrupted by processing techniques such as thermoforming and extrusion of plastics and drawing of fibers. In the last process, which is descriptive of the others, the crystallites are ordered in the direction of the stress, the filament shrinks in diameter, and heat is evolved and reabsorbed as a result of additional orientation and crystallization.

In addition to crystallization of the backbone of polymers, crystallization may also occur in regularly spaced bulky groups even when an amorphous structure is maintained in the backbone. In general, the pendant group must contain at least 10 carbon atoms in order for this side chain crystallization to occur. Ordered polymers with small pendant groups crystallize more readily than those with bulky groups.

While polymeric hydrocarbons have been used as illustrations for simplicity, it is important to note that the principles discussed apply to all polymers, organic as well as inorganic, and natural as well as synthetic, and to elastomers, plastics, and fibers.

2.4 AMORPHOUS BULK STATE

An amorphous bulk polymer contains chains that are arranged in something less than a well-ordered, crystalline manner. Physically, amorphous polymers exhibit a T_g but not a T_m and do not give a clear x-ray diffraction pattern. Amorphous polymer chains have been likened to spaghetti

strands in a pot of spaghetti, but in actuality the true extent of disorder that results in an amorphous polymer is still not fully understood.

Section 12.3 contains a discussion of a number of techniques employed in the search for the real structure of the amorphous bulk state. Briefly, evidence suggests that little order exists in the amorphous state, the order being similar to that observed with low-molecular-weight hydrocarbons. There is evidence that there is some short-range order and for long-range interactions and that the chains approximate a random coil with some portions paralleling one another. In 1953, Flory and Mark suggested a random coil model whereby the chains had conformations similar to those present if the polymer were in a theta solvent. In 1957, Kargin suggested that amorphous polymer chains exist as aggregates in parallel alignment. Models continue to be developed, but all contain the elements of disorder/order suggested by Flory and Mark and the elements of order suggested by Kargin.

2.5 POLYMER STRUCTURE–PROPERTY RELATIONSHIPS

Throughout the text we will relate polymer structure to the properties of the polymer. Polymer properties are related not only to the chemical nature of the polymer but also to such factors as extent and distribution of crystallinity, distribution of polymer chain lengths, and nature and amount of additives, such as fillers, reinforcing agents, and plasticizers, to mention a few. These factors influence essentially all the polymeric properties to some extent including hardness, flammability, weatherability, chemical stability, biological response, comfort, flex life, moisture retention, appearance, dyeability, softening point, and electrical properties.

Materials must be varied to perform the many tasks required of them in today's society. Often they must perform them repeatedly and in a "special" manner. We get an ideal of what materials can do by looking at some of the behavior of giant molecules in our body. While a plastic hinge must be able to work thousands of times, the human heart, a complex muscle largely composed of protein polymers (Section 4.7), provides about 2.5 billion beats within a lifetime moving oxygen (Section 11.8) throughout the approximately 144,000 km of the circulatory system with (some) blood vessels the thickness of hair and delivering about 8000 L of blood every day with little deterioration of the cell walls. The master design allows nerve impulses to travel within the body at the rate of about 300 m/min; again polymers are the "enabling" material that allows this rapid and precise transfer of nerve impulses. Human bones, again largely polymeric, have strength about five times that of steel (on a weight basis). Genes, again polymeric (Section 4.8), appear to be about 99.9% the same between humans, with the 0.1% functioning to give individuals the variety of size, abilities, etc., which confer uniqueness. In the synthetic realm, we are beginning to understand and mimic the complexities, strength, preciseness, and flexibility that are already present in natural polymers.

Here we will briefly deal with the chemical and physical nature of polymeric materials that permit their division into three broad divisions—elastomers or rubbers, fibers, and plastics. *Elastomers* are high polymers possessing chemical and/or physical cross-links. For industrial application, the "use" temperatures must be above T_g (to allow for ready "chain" mobility), and its normal state (unextended) must be amorphous. The restoring force, after elongation, is largely due to entropy. On release of the applied force, the chains tend to return to a more random state. Gross, actual mobility of chains must be low. The cohesive energy forces between chains should be low permitting rapid, easy expansion. In its extended state, a chain should exhibit a high tensile strength, whereas at low extensions, it should have a low tensile strength. Cross-linked vinyl polymers often meet the desired property requirements. The material, after deformation, should return to its original shape because of the cross-linking. This property is often referred to as an elastic "memory." Figure 2.18 illustrates force versus elongation for a typical elastomer. As the elastomer is pulled, the largely random chain segments become "stretched out" forming microcrystalline domains. Eventually, most of the chains are part of these microcrystalline domains resulting in further elongation requiring much increased force (stress). This microcrystallization also confers to the elastomer a greater brittleness, eventually resulting in the rubber breaking as additional stress is applied.

Fiber properties include high tensile strength and high modulus (high stress for small strains). These properties can be obtained from high molecular symmetry and high cohesive energies

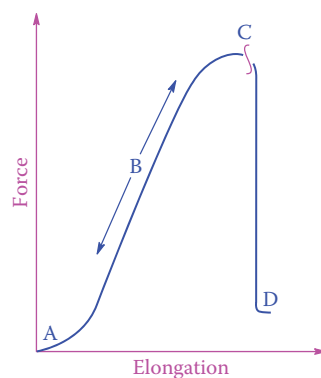


FIGURE 2.18 Elongation of an elastomer as a function of applied force, stress, where A is the original “relaxed” state, B represents movement to full extension, C is the point at which the elastomer “breaks,” and D represents force necessary to pull two separate pieces of elastomer apart.

between chains, both requiring a fairly high degree of polymer crystallinity. Fibers are normally linear and drawn (oriented) in one direction, producing higher mechanical properties in that direction. Typical condensation polymers, such as polyesters and nylons, often exhibit these properties. If the fiber is to be ironed, its T_g should be above 200°C , and if it is to be drawn from the melt, its T_g should be below 300°C . Branching and cross-linking are undesirable since they disrupt crystalline formation, even though a small amount of cross-linking may increase some physical properties, if effected after the material is drawn and processed. Permanent press garments often have some cross-linking ensuring a “remembrance” of the “permanent press.”

Products with properties intermediate between elastomers and fibers are grouped together under the heading “**plastics**.”

Selected property–structure relationships are summarized in Tables 2.6 and 2.7. As noted before, some polymers can be classified in two categories, with properties being greatly varied by varying molecular weight, end group, processing, cross-linking, plasticizer, and so on. Nylon 66 in its more crystalline form behaves as a fiber, whereas less crystalline forms of nylon 66 are generally classified as plastics.

Many polymers can be treated to express more than one behavior. As noted earlier, nylon 66 provides good fibrous material when aligned and behaves as a plastic if it is not aligned. Polyesters also exhibit the same tendencies. Other materials, such as PVC and siloxanes, can be processed to act as plastics or elastomers.

TABLE 2.6 Selected Property–Structure Relationships

<i>Glass transition temperature</i>	<i>Solubility</i>
Increases with the presence of	Favored by
Bulky pendant groups	Longer chain lengths
Stiffening groups as 1,4-phenylene	Low interchain forces
Chain symmetry	Disorder and dissymmetry
Polar groups	Increased temperature
Cross-linking	Compatible solvent
Decreases with the presence of	<i>Crystallinity</i>
Additives like plasticizers	Favored by
Flexible main chain groups	High interchain forces
Nonpolar groups	Regular structure; high symmetry
Dissymmetry	Decrease in volume
	Increased stress
	Slow cooling from melt
	Homogeneous chain length

TABLE 2.7 General Property Performance–Structure Relationships^a

	Increased Crystallinity	Increased Cross-Linking	Increased Mol. Wt.	Increased Mol. Wt. Distribution	Addition of Polar Backbone Units	Addition of Backbone Stiffening Groups
Abrasion resistance	+	+	+	–	+	–
Brittleness	–	M	+	+	+	+
Chemical resistance	+	V	+	–	–	+
Hardness	+	+	+	+	+	+
T _g	+	+	+	–	+	+
Solubility	–	–	–	0	–	–
Tensile strength	+	M	+	–	+	+
Toughness	–	–	+	–	+	–
Yield	+	+	+	+	+	+

^a +, increase in property; 0, little or no effect; –, decrease in property; M, property passes through a maximum; V, variable results dependent on particular sample and temperature.

2.6 CRYSTALLINE AND AMORPHOUS COMBINATIONS

Most polymers consist of a combination of crystalline and amorphous regions. Even within polymer crystals such as spherulites (Figures 2.15 through 2.17), the regions between the ordered folded crystalline lamellae are less ordered, approximating amorphous regions. This combination of crystalline and amorphous regions is important for the formation of materials that have both good strength (contributed largely by the crystalline regions) and some flexibility or “softness” (derived from the amorphous portions). Figure 2.16 contains a space-filled model for PE chains (a total of about 400 units with 5 branches, 1 longer and 4 shorter).

This model of PE contains a mixture of amorphous and crystalline regions. Note the cavities within the amorphous regions with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of the crystalline regions are referred to as being crystalline, and they are less flexible and stronger and offer better stability to nature and attack by acids and bases, oils, etc. Also as noted before, amorphous regions give the material flexibility while the crystalline regions give the material strength. Thus, many materials contain both crystalline and amorphous regions giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

Through the use of specific treatment(s), the crystalline/amorphous regions can vary from being largely random to being preferentially oriented in one direction with a greater degree of “crystalline-type” structures when unidirectional stress is applied (Figure 2.19). Here the amount of free space or volume is less with the overall order greater and properties associated with these changes also changed. The material will be stronger and have a greater ability to resist attack by acids, bases, oils, and other external agents, and the diffusion of gases and other agents through it is less. Polymers can be oriented (such as the pulling of fibers or films) in one or two directions. This preferential orientation results in the fiber or film material with anisotropic properties, with the material showing greater strength along the axis of pull.

Figure 2.20 shows the general relationship between material “hardness/softness” and the proportion that is crystalline for largely linear polymers.

There are some general guidelines with respect to a materials, T_g and T_m, its general amorphous/crystalline structure, and the potential use area. *Elastomers* are cross-linked, amorphous polymers where the use temperature is above its T_g. An *adhesive* is a linear or branched amorphous polymer that is used above its T_g. *Coatings* are generally near their T_g when used so that some flexibility is present allowing the coatings material to withstand temperature changes

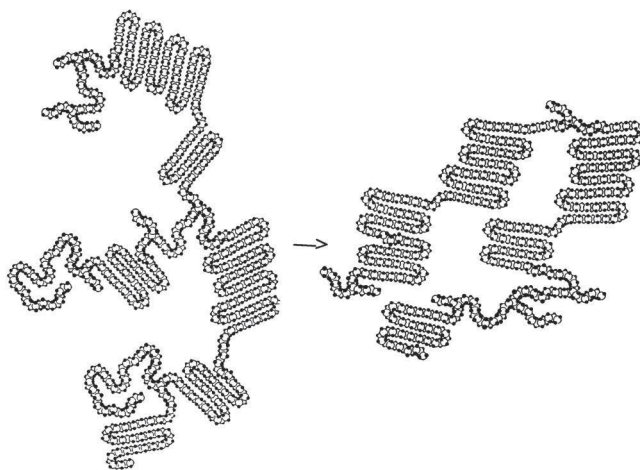


FIGURE 2.19 Idealized structure illustrating crystalline (ordered) and amorphous (nonordered) regions of lightly branched polyethylene chains for a prestressed and stressed orientation.

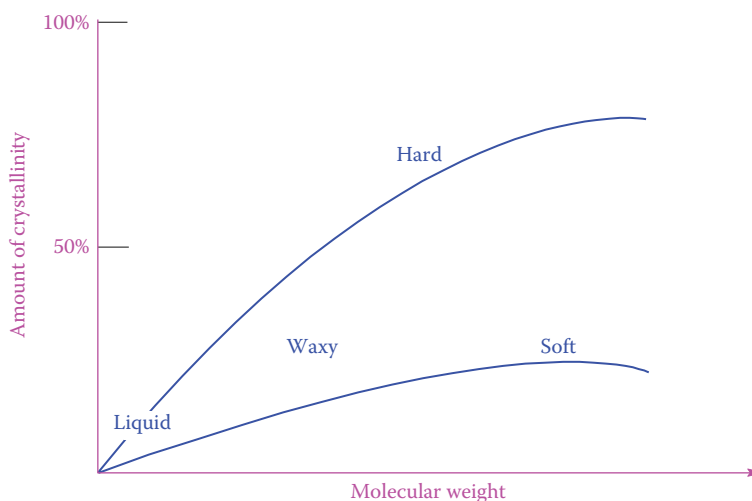


FIGURE 2.20 General physical states of materials as a function of crystallinity and molecular weight.

without cracking and so coalescing occurs on drying. *Plastics* can be either amorphous or partially amorphous. Amorphous (or partially crystalline) plastics such as PP and PE should have a use temperature below the T_m but above the T_g . *Fibers* are composed of crystalline polymers where the use temperature is below the T_m . These general dependencies of properties related to T_g are summarized in Table 2.8.

TABLE 2.8 General Property Correlations with T_g

Cross-linked elastomers	Above T_g
Linear (or branched) amorphous adhesives	Above T_g
Amorphous plastics	Generally above T_g
Largely crystalline plastics	Generally above T_g , below T_m
Crystalline fibers	Below T_m
Coatings	At or near T_g

2.7 CROSS-LINKING

Cross-linking is important since it can lock in structures, give structures “memory,” and greatly impact the physical properties. Cross-linking can be divided into three general types. Chemical cross-linking consists of the formation of primary ionic or covalent bonds that connect various chains. Such cross-linking can be intentional such as formation of sulfur cross-links in many elastomers connecting chains giving the cross-linked material “memory” as well as other properties. Here, the cross-linking is referred to as “vulcanizing” and “curing” (Figure 2.21). For the hair, the breakage and formation of thiol cross-linking is involved with permanents, and the term “setting” is often employed to describe this process. Primary bond formation is also responsible for making some polymers unintentionally brittle through exposure to UV sunlight. Primary chemical bond formation through cross-linking often leads to the formation of thermoset materials. Chemical cross-linking can result from heat, light, exposure to chemicals, etc.

The two main types of physical cross-linking are illustrated in Figure 2.22. One method involves chain entanglement. Just as with string and yarn, the longer the strands, the more apt they are to entangle. As one attempts to pull a single strand, other strands are pulled along. This is analogous to what occurs with polymer chains. For long chains, because of chain entanglement as one chain is pulled, other chains are also tugged on resulting in a great increase in the apparent chain length. Many properties such as tensile strength are dependent on the chain length and such properties see a marked increase as chain entanglement begins. For many polymers, such chain entanglement begins as the chain length approaches 100 units.

The second type of physical cross-linking involves formation of crystalline portions within an amorphous grouping. For vinyl polymers, the temperature that allows segmental chain mobility to occur is well below room temperature, but the temperature to disrupt crystalline formations is typically well above room temperature. Within mixtures of crystalline and amorphous structures below the T_m , the crystalline portions act to “tie-in” or connect the surrounding areas acting as

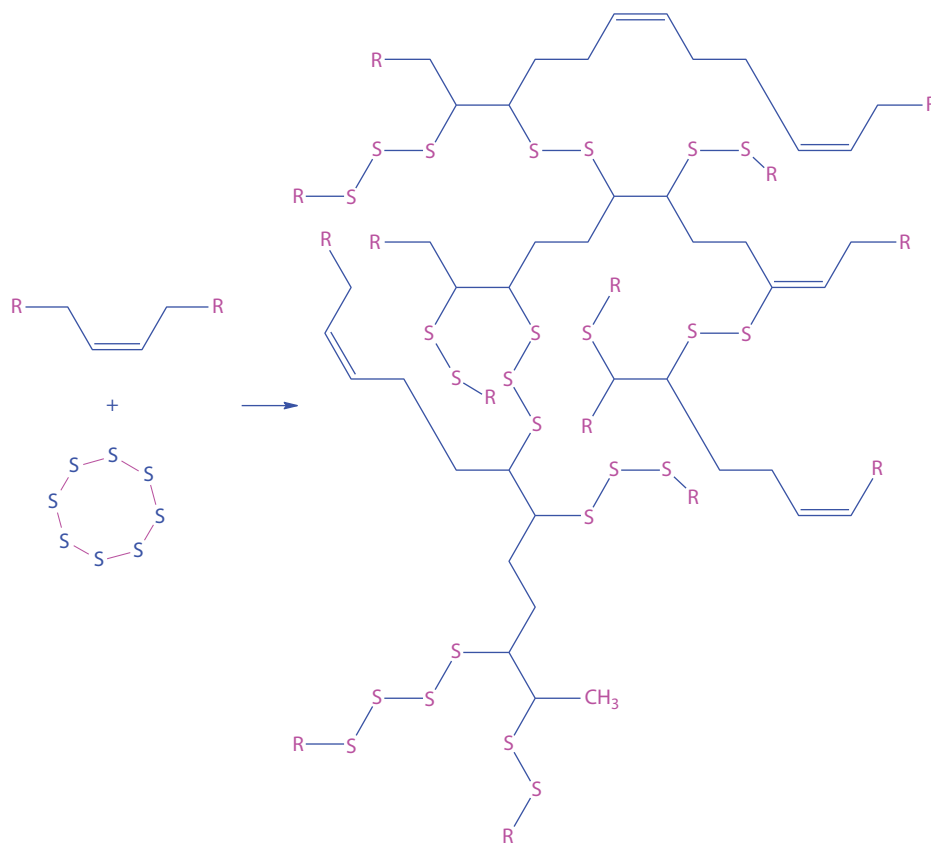


FIGURE 2.21 Chemical cross-linking of *cis*-1,4-butadiene through reaction with sulfur.

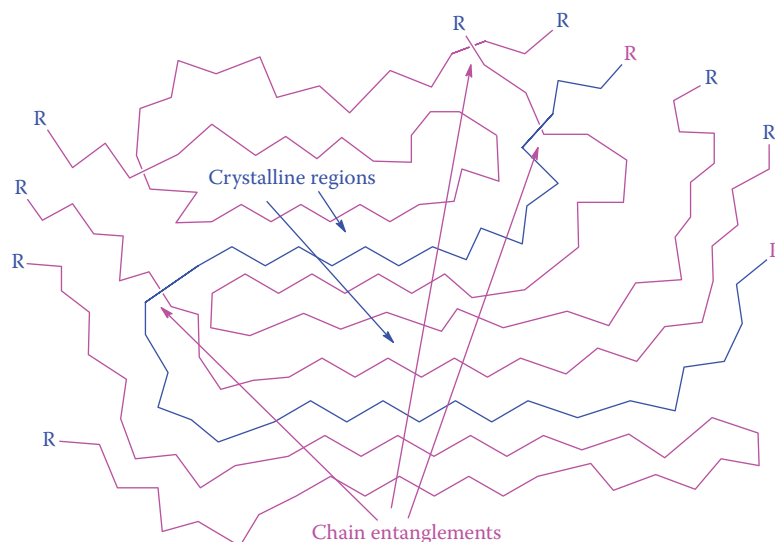


FIGURE 2.22 Illustration of two types of physical cross-linking—chain entanglement and crystalline regions.

cross-links. Formation of secondary bonding cross-linking is a primary method to retain desired 3D structures (conformations) in proteins and nucleic acids. This secondary bonding generally entails a variety of forces including hydrogen-bonding and the formation of such structures can also involve formation of crystalline regions such as within nylons and polyesters.

The general name given to materials that do not melt when heated is “**thermoset**.” Thermoset materials generally contain chemical cross-links. Since they do not melt when heated, it is more difficult to recycle such materials. By comparison, materials that do melt when heated are called “**thermoplastics**.” Such materials do melt when heat is applied and so are more easily recycled. Examples of thermosets are some elastomers and phenolic and amino plastics. Polystyrene, PP, PE, nylon, and polyesters are examples of thermoplastic materials. By weight and value, we use many more synthetic thermoplastic materials. Even so, both thermoset and thermoplastic materials can be recycled.

SUMMARY

1. Polymers or macromolecules are high-molecular-weight compounds with chain lengths greater than the critical length required for the entanglement of these chains. There is an abrupt change in melt viscosity and other physical properties of high-molecular-weight polymers when the chain length exceeds the critical chain length.
2. While some naturally occurring polymers, such as proteins, are monodisperse, that is, all have the same molecular weight, other natural and synthetic polymers, such as cellulose and PE, are polydisperse, that is, they consist of a mixture of chains of differing numbers of units. Thus one uses the term average molecular weight when describing the molecular weight of these polydisperse materials.
3. Many polymers, such as cellulose and HDPE, are linear polymers containing long, continuous, covalently bonded atoms. Others may be branched or cross-linked. Both linear polymers and those with branching are generally thermoplastics that can be remolded by application of heat and pressure. Others that are cross-linked are thermosets that cannot be remolded by application of heat and pressure. Both groups of polymers can be recycled, but it is easier to recycle thermoplastic materials.
4. Groups off the polymer backbone, such as the methyl group in PP, are called pendant groups. Such polymers are formed giving mainly a head-to-tail arrangement rather than a head-to-head arrangement.
5. The temperature at which local segmental mobility occurs is called the T_g and where wholesale polymer chain mobility occurs is called the T_m .

6. The first-order transition or melting point (T_m) is energy wise larger than the T_g . Entirely crystalline polymers will have only a T_m , whereas a totally amorphous polymer will have only a T_g . Since most polymers are a combination of amorphous and crystalline regions, they have both a T_g and a T_m .
7. A polymer stretched out to its full contour length is only one of the myriad conformations possible for a polymer. The chain length is expressed statistically as the root-mean-square distance that is only a fraction of the contour length.
8. Since branched chains like LDPE have many chain ends, it is customary to use the radius of gyration, S , as a measure of the distribution of polymer segments. The radius of gyration is the distance of a chain end from the polymer's center of gravity rather than a measure of the root-mean-square. Both measures are statistically related.
9. Fibers and stretched elastomers are translucent because of the presence of ordered crystallites or regions of crystallinity.
10. Crystalline regions of polymers can be represented as combinations of folded chains forming lamellar structures. Amorphous regions are less ordered than crystalline regions. Additional orientation of polymer chains occurs when stress is applied resulting in increased strength in the direction of the applied stress. This results in increased strength in the order of the orientation.
11. The principal differences between elastomers, plastics, and fibers are the presence and absence of stiffening groups, molecular symmetry, and the strength of the intermolecular forces. Elastomers are typically characterized by the absence of stiffening groups, the presence of molecular asymmetry, low amount of crystallinity, and overall absence of strong intermolecular forces. In contrast, fibers are characterized by the presence of stiffening groups, molecular symmetry, high amount of crystallinity, and the presence of strong intermolecular forces. Fibers have a lack of branching and irregularly spaced pendant groups. Plastics have structures and properties that are between elastomers and fibers.
12. There are three types of cross-linking. Cross-linked materials have good dimensional memory. The types of cross-linking are chemical and two physical types of cross-linking. Physical cross-linking results from formation of crystalline regions within polymer structures and from chain entanglement. Chemically cross-linked materials do not dissolve and they do not melt.

GLOSSARY

Amorphous: Noncrystalline polymer or region in a polymer.

Atactic: Polymer in which there is a random arrangement of pendant groups on each side of the chain.

Backbone: Principal chain in a polymer.

Branched polymer: Polymer having extensions attached to the polymer backbone. Not pendent groups.

Bulky groups: Sterically large groups.

Chiral center: Asymmetric center such as a carbon atom with four different groups attached to it.

Cold drawing: Stretching a fiber under room temperature.

Configurations: Related chemical structures produced by the breaking and remaking of primary covalent bonds.

Conformations: Various shapes of polymer chains resulting from the rotation about single bonds in the polymer chain.

Conformer: Shape produced by a change in the conformation of a polymer.

Contour length: Fully extended length of a polymer chain; equal to the product of the length of a repeat unit times the number of units, or mers.

Critical chain length (z): Minimum chain length required for entanglement of polymer chains.

Cross-linked density: Measure of the relative degree of cross-linking.

Crystalline polymer: Polymer with ordered structure.

Crystallites: Regions of crystallinity.

Degree of polymerization: Number of repeat units in a chain.

Dipole–dipole interactions: Moderate secondary forces between polar groups in different or the same polymer chain.

Dispersion forces: Low-energy secondary forces due to the creation of momentary-induced dipoles; also known as London forces.

Glass transition temperature (T_g): Temperature range where a polymer gains local or segmental mobility.

Glassy state: Hard, brittle state; below T_g .

Gutta percha: Naturally occurring trans isomer of polyisoprene.

Heat-to-tail configuration: Normal sequence of mers in which the pendant groups are regularly spaced; for PVC, the chlorine atom appears on every other carbon.

High-density polyethylene (HDPE): Largely linear polyethylene.

Intermolecular forces: Secondary forces between different molecules.

Intramolecular forces: Secondary forces within the same molecule.

Isotactic: Polymer where the geometry of the pendent groups is all on the same side of the polymer backbone.

Lamellar: Platelike, or planar (flat), in shape.

Linear polymer: Polymer without chains extending off the backbone.

Linear, low-density polyethylene (LLDPE): Does not contain long branching; copolymer of ethylene and α -olefins.

Low-density polyethylene (LDPE): A branched form of PE produced at high pressure by the free-radical-initiated polymerization of ethylene.

Maltese cross: Cross with arms like arrowheads pointing inward.

Melting point (T_m): First-order transition when the solid and liquid phases are in equilibrium.

Mer: Repeat unit.

Modulus: Ratio of stress to strain, which is a measure of the stiffness of a polymer.

Monodisperse: Polymer mixture made up of molecules of one specific molecular weight.

Pendant groups: Groups attached to the main polymer backbone, like methyl groups in polypropylene.

Polydisperse: Polymer mixture containing chains of varying lengths.

Radius of gyration (S): Root-mean-square distance of a chain end to a polymer's center of gravity.

Root-mean-square distance [$\langle r^2 \rangle^{1/2}$]: Average end-to-end distance of polymer chains; $l(n^{1/2})$.

Side chain crystallization: Crystallization related to that of regularly spaced long pendant groups.

Single polymer crystals: Lamellar structure consisting of folded chains of a linear polymer.

Spherulites: Three-dimensional aggregates of polymer crystallites.

Stiffening groups: Groups in a polymer backbone that decrease the segmental motion of the polymer chain.

Syndiotactic: Polymer in which the pendant groups are arranged alternately on each side of the carbon backbone.

Tacticity: Arrangement of the pendant groups in space; that is, isotactic, syndiotactic, and atactic.

Thermoplastic: A linear polymer that softens when heated.

Thermoset: A network polymer containing chemical cross-linking that does not soften when heated.

Ultrahigh-molecular-weight polyethylene (UHMWPE): High molecular weight largely linear polyethylene.

Van der Waals forces: Secondary forces based on the attraction between groups.

Viscosity: Measure of the resistance of a polymer or polymer solution to flow.

EXERCISES

(To answer some of these questions, you may need to look at other parts in the book for structures and specific details.)

1. Make sketches or diagrams showing (a) a linear polymer, (b) a polymer with pendant groups, (c) a polymer with short branches, (d) a polymer with long branches, and cross-linked polymers with (e) low and (f) high cross-linked density.
2. Which has (a) the greater volume for the same weight of material and (b) the lower softening point: HDPE or LDPE?

3. What is the approximate bond length of the carbon atoms in (a) a linear and (b) a cross-linked polymer?
4. What is the approximate contour length of an HDPE chain with an average degree of polymerization (chain length) of $n = 2000$ and of a PVC chain of the same number of repeating units?
5. Which of the following are monodisperse polymers with respect to chain length: (a) *Hevea* rubber, (b) corn starch, (c) cellulose from cotton, (d) an enzyme, (e) HDPE, (f) PVC, (g) a specific DNA, (h) nylon 66, or (i) a specific RNA?
6. What is the average degree of polymerization of LDPE having an average molecular weight of 28,000?
7. What is the structure of the repeating unit in (a) polypropylene, (b) poly(vinyl chloride), and (c) *Hevea* rubber?
8. Which of the following is a branched chain polymer: (a) HDPE, (b) isotactic PP, (c) LDPE, or (d) amylose starch?
9. Which of the following is a thermoplastic: (a) ebonite, (b) Bakelite, (c) vulcanized rubber, (d) HDPE, (e) celluloid, (f) PVC, or (g) LDPE?
10. Which has the higher cross-linked density: (a) ebonite or (b) soft vulcanized rubber?
11. Do HDPE and LDPE differ in (a) configuration or (b) conformation?
12. Which is a trans isomer: (a) gutta percha or (b) *Hevea* rubber?
13. Which will have the higher softening point: (a) gutta percha or (b) *Hevea* rubber?
14. Show (a) a head-to-tail and (b) a head-to-head configuration for PVC.
15. Show the structure of a typical portion of the chain of (a) s-PVC and (b) i-PVC.
16. Show Newman projections of the gauche forms of HDPE.
17. Name polymers whose intermolecular forces are principally (a) London forces, (b) dipole–dipole forces, and (c) hydrogen bonding.
18. Which will be more flexible: (a) poly(ethylene terephthalate) or (b) poly(butylene terephthalate)?
19. Which will have the higher glass transition temperature: (a) poly(methylene methacrylate) or (b) poly(butyl methacrylate)?
20. Which will have the higher T_g : (a) i-PP or (b) a-PP?
21. Which will be more permeable to a gas at room temperature: (a) i-PP or (b) a-PP?
22. Under what kind of physical conditions is a linear polymer more apt to form spherulites?
23. What is the full contour length of a molecule of HDPE with a DP of 1500?
24. Which would be more flexible: (a) poly(methyl acrylate) or (b) poly(methyl methacrylate)?
25. Which would you expect to form “better” helical structures: (a) i-polypropylene or (b) a-polypropylene?
26. Which would you expect to have a higher melting point: (a) nylon 66 or (b) an aramide?
27. What type of hydrogen bonds are present in the internal structure of a globular protein?
28. Which would have the greater tendency to “cold flow” at room temperature: (a) poly(vinyl acetate) ($T_g = 301\text{ K}$) or (b) polystyrene ($T_g = 375\text{ K}$)?
29. Which would be least transparent: (a) combination of amorphous and crystalline PS, (b) entirely crystalline PS, or (c) entirely amorphous PS?
30. Which would be more apt to produce crystallites: (a) HDPE or (b) poly(butyl methacrylate)?
31. Which of the following would you expect to provide strong fibers (a) nylon 66, (b) a-polypropylene, or (c) wool?
32. Which would tend to be more crystalline when stretched: (a) unvulcanized rubber or (b) ebonite?
33. Which would be more apt to exhibit side chain crystallization: (a) poly(methyl methacrylate) or (b) poly(dodecyl methacrylate)?
34. What must be present in order for movement to occur within a polymer at T_g or T_m ?
35. What are the three major forms of cross-linking?

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Molecular Weight of Polymers

3.1 INTRODUCTION

It is the size of macromolecules that gives them their unique and useful properties. Size allows polymers to act more as a group so that when one polymer chain moves, surrounding chains are affected by that movement. Size also allows polymers to be nonvolatile since the secondary attractive forces are cumulative (for instance, London dispersion forces are about 8 kJ/mol per repeat unit), and because of the sheer size, the energy necessary to volatilize them is sufficient to degrade the polymer.

Generally, the larger the polymer, the higher the molecular weight. The average molecular weight (M) of a polymer is the product of the average number of repeat units or mers expressed as DP times the molecular weight for the repeating unit. Thus, for polyethylene (PE) with an average DP of 100, the average molecular weight is simply 100 units times 28 daltons/unit = 2800 daltons (Da). Note that amu and daltons refer to equivalent units.

Polymerization reactions, both synthetic and natural (but not for all natural materials such as proteins and nucleic acids), lead to polymers with heterogeneous molecular weights, that is, polymer chains with different numbers of mers. Molecular weight distributions (MWDs) may be rather broad (Figure 3.1), relatively narrow, or may be mono-, bi-, tri-, or polymodal. A bimodal curve is often characteristic of a polymerization occurring under two different environments. Polymers consisting of chains of differing lengths are called polydisperse, while polymers containing only one chain length, such as specific nucleic acids, are called monodisperse.

Many physical properties are related to molecular weight. Figure 3.2 lists three of these. The melt viscosity is typically proportional to the 3.4 power of the average chain length; so melt viscosity, η , is proportional to $M^{3.4}$. Thus, the melt viscosity increases rapidly as the chain length increases, and more energy is required for the processing and fabrication of large molecules. However, there is a trade-off between molecular weight-related properties and chain size such that there is a range where acceptable physical properties are present but the energy required to cause the polymers to flow for processing is acceptable. This range is called the “commercial polymer range.” As seen in Figure 3.2, many physical properties tend to level off at some point and increased chain length gives little increase in that physical property. Thus, most commercial polymer ranges include the beginning of this leveling off threshold.

While a value above the *threshold molecular weight value* (TMWV; lowest molecular weight where the desired property value is achieved) is essential for most practical applications, the additional cost of energy required for processing extremely high polymer molecular weights is seldom justified. Accordingly, it is customary to establish a commercial polymer range above the TMWV but below the extremely high-molecular-weight range. However, it should be noted that since toughness increases with chain length, extremely high-molecular-weight polymers, such as ultrahigh molecular weight polyethylene (UHMPE), are used for the production of tough articles such as waste barrels.

Some properties are not as sensitive to molecular weight such as heat capacity, refractive index, and density. Even so, many important properties are related to chain length.

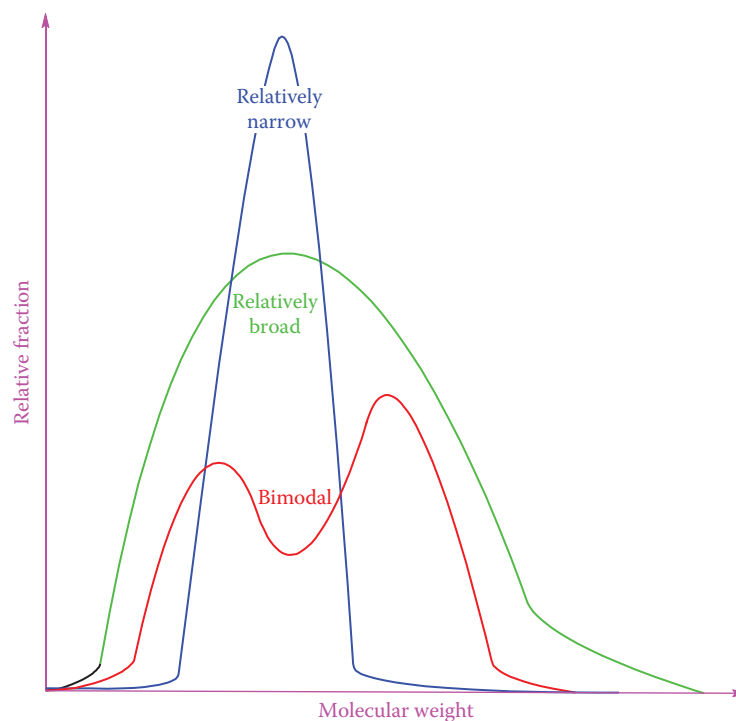


FIGURE 3.1 Relative differential weight distribution curves.

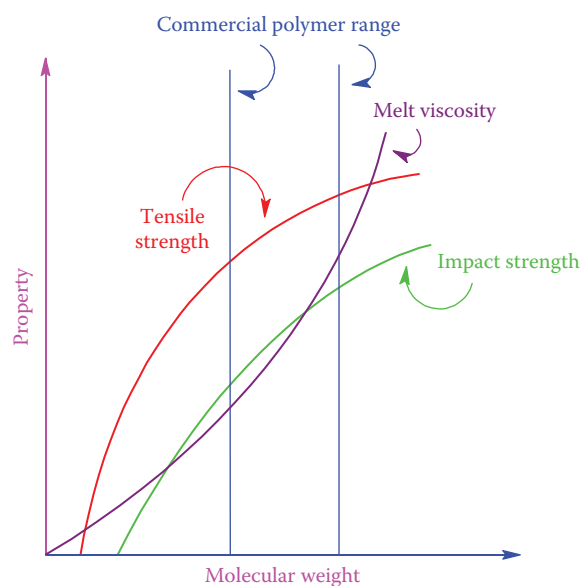


FIGURE 3.2 Relationship between molecular weight and polymer physical properties.

Oligomers and other low-molecular-weight polymers are not useful for applications where high strength is required. The word oligomer is derived from the Greek word *oligos*, meaning *a few*.

The value of TMWV is dependent on T_g , the cohesive energy density (CED) of amorphous polymers, the extent of crystallinity in crystalline polymers, and the effect of reinforcements in polymeric composites. Thus, while a low-molecular-weight amorphous polymer may be satisfactory for use as a coating or adhesive, a chain length generally above 100 may be required if the polymer is to be used as an elastomer or plastic.

3.2 SOLUBILITY

3.2.1 BASIC CONCEPTS

Solubility of biologically important macromolecules as some proteins and nucleic acids is not straight forward since they often behave micelle or colloid-like and are said to be soluble in water. These essential molecules have a different hydrophobic inner structure and hydrophilic outer structure designed allowing them to function within an aqueous environment yet maintain the essential inner structure retaining the critical geometries necessary to perform various activities.

Polymer mobility is important in a number of aspects. Most processing procedures require a polymer to be fluid enough, either through application of heat and/or pressure or with the polymer present in a solution, to be processed. Here, we will focus on the general topic of polymer solubility and factors that influence polymer solubility.

Polymer mobility is an important aspect helping determine a polymer's physical, chemical, and biological behavior. Lack of mobility, either because of interactions that are too swift to allow the segments within the polymer chain some movement or because there is not sufficient energy (such as a high enough temperature) available to create mobility or because of a lack of available free volume, results in a brittle material. Many processing techniques require the polymer to have some mobility. This mobility can be achieved through application of heat and/or pressure and through dissolving the polymer. Because of its size, the usual driving force of entropy increase for the mixing and dissolving of materials is smaller for polymers in comparison to small molecules. Traditional molecular weight determinations require that the polymer be dissolved.

The physical properties of polymers, including solubility, are related to the strength of covalent bonds, the stiffness of the segments in the polymer backbone, the amount of crystallinity/amorphous, and the intermolecular forces between the polymer chains. The strength of the intermolecular forces is equal to the Cohesive Energy Density (CED), which is the molar energy of vaporization per unit volume. Since intermolecular attractions of solvent and solute must be overcome when a solute (here the polymer) dissolves, CED values may be used to predict solubility.

When a polymer dissolves, the first step is often a slow swelling process called solvation in which the polymer molecules swell by a factor δ , which is related to CED. Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition.

In order for a material to be dissolved, it is essential that the free energy difference which is the driving force in the solution process, decrease to below zero, that is, be negative. ΔH and ΔS are equal to the change in enthalpy and change in entropy, and for constant temperature, the relationship is the classical Gibbs equation:

$$(3.1) \quad \Delta G = \Delta H - T\Delta S$$

“Like-likes-like best of all” is a description that is useful at appropriate times in science. It is true of solubility. Thus, water-likes-water best of all and is infinitely soluble in itself. Hexane-likes-hexane best of all and is infinitely soluble in itself. Hexane and water are not soluble in one another because hexane is nonpolar and water is polar; thus, they are not *like one another*. In solubility, and in fact all mixing, the ΔH term is always unfavorable when mixing or solubility occurs. (Shortly, we will deal with attempts such as the CED and solubility parameter to minimize the unfavorable aspect of the ΔH term.) Thus, it is the ΔS term that allows mixing and solubility to occur. As seen in Figure 3.3, the amount of randomness or disorder gain is great when pure materials such as water and ethanol are changed from the ordered pure materials to the disordered mixture.

By comparison, the increase in randomness, ΔS , is much smaller if one of the materials is a polymer since the possible arrangements of the polymer chains is much more limited because the polymer units are attached to one another and not free to simply move about on their own. Figure 3.4 illustrates this with water and poly(ethylene glycol) (PEG). We notice several aspects. First, as noted earlier, the number of arrangements of the PEG units is limited. Second, as in the case of an onion, each layer of PEG chains must be peeled back allowing water molecules to approach inner layers before entire solubility occurs and causes swelling. This results in polymer

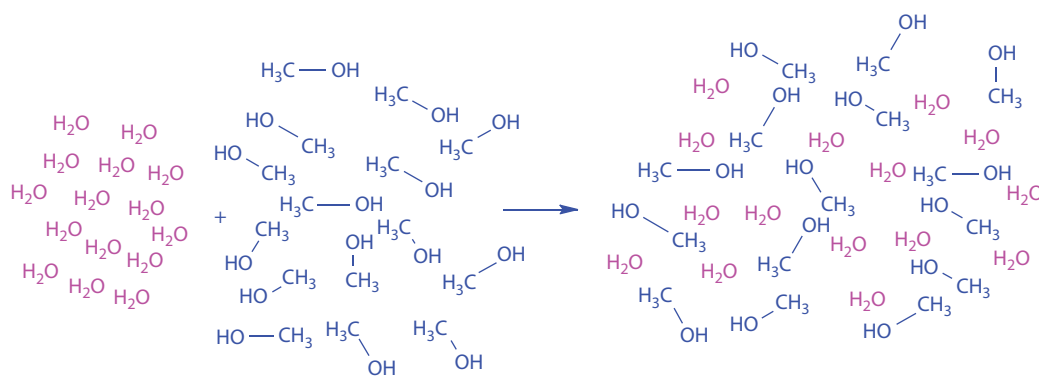


FIGURE 3.3 Illustration of the mixing of small molecules.

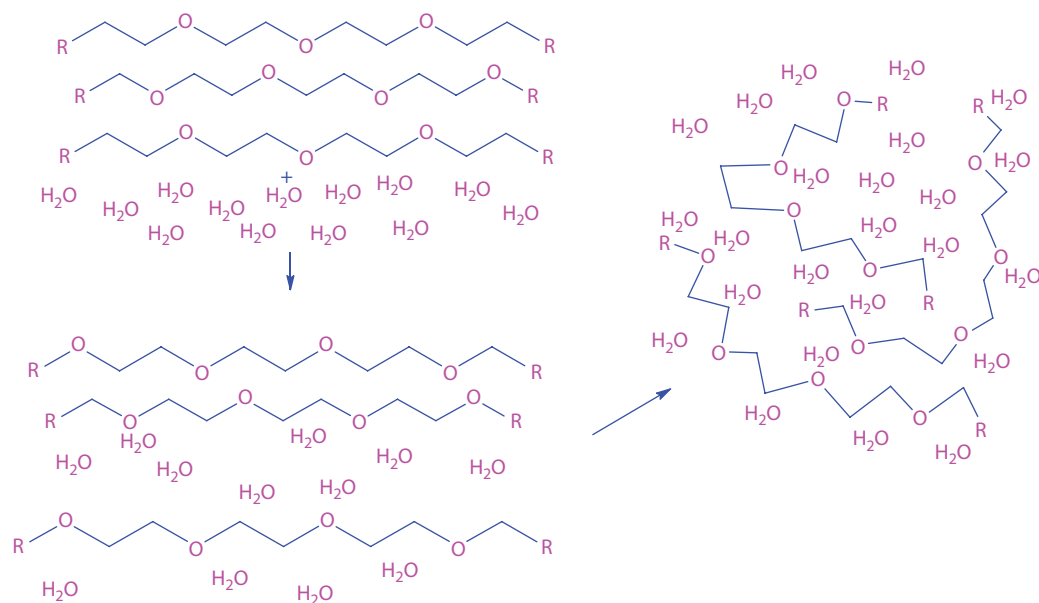


FIGURE 3.4 Illustration of water dissolving poly(ethylene glycol).

solubility often requiring a longer period of time, sometimes hours to weeks to months, in comparison to the solubility of smaller molecules where solubility can occur in seconds.

Polymer solubility, in comparison to small molecules, is:

- More limited with respect to the number of solvents as a result of the lower increase in randomness that must overcome the unfavorable enthalpy term
- More limited with respect to the extent of solubility
- Takes a longer time to occur

The *theta* (θ) *temperature* is the lowest temperature at which a polymer of infinite molecular weight is completely miscible with a specific solvent. The polymer coil expands above the theta temperature and contracts at lower temperatures.

3.2.2 THEORETICAL APPROACHES TO SOLUBILITY

As early as 1926, Hildebrand showed a relationship between solubility and the internal pressure of the solvent and in 1931 Scatchard incorporated the CED concept into Hildebrand's equation. This led to the concept of a *solubility parameter* that is the square root of CED. Thus, as shown

in (3.2), the solubility parameter δ for nonpolar solvents is equal to the square root of the heat of vaporization per unit volume:

$$(3.2) \quad \delta = \left(\frac{\Delta E}{V} \right)^{1/2} = (\text{CED})^{1/2} \quad \text{or} \quad \delta^2 = \text{CED}$$

According to Hildebrand, the heat of mixing a solute and a solvent is proportional to the square of the difference in solubility parameters, as shown in (3.3), where ϕ is the partial volume of each component, namely, solvent ϕ_1 and solute ϕ_2 . Since typically the entropy term favors solution and the enthalpy term acts counter to solution, the objective is to match solvent and solute so that the difference between their δ values is small:

$$(3.3) \quad \Delta H_m = \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

The solubility parameter concept predicts the heat of mixing liquids and amorphous polymers. Hence, any nonpolar amorphous polymer will dissolve in a liquid or mixture of liquids having a solubility parameter that generally does not differ by more than ± 1.8 (cal/cm³)^{1/2}. The Hildebrand (H) with units of (cal/cm³)^{1/2} is preferred over these complex units giving that mixing occurs when the heat of mixing is within the range of ± 1.8 H.

Because the law of mixtures applies to the solubility parameter, it is possible to blend non-solvents forming mixtures that can serve as solvents. For example, an equimolar mixture of *n*-pentane ($\delta = 7.1$ H) and *n*-octane ($\delta = 7.6$ H) will have a solubility parameter value of 7.35 H.

The solubility parameter of a polymer is generally determined by noting the extent of swelling or actual solution of small amounts of polymer in a series of solvents and comparing the solubility values of the ones that swell or dissolve the polymer and assigning the polymer a solubility parameter value that is close to the solvents that dissolve/swell the polymer. The solubility

TABLE 3.1 Solubility Parameters (δ) for Typical Solvents

Poor Hydrogen Bonding		Moderate Hydrogen Bonding		Strong Hydrogen Bonding	
Dimethylsiloxane	5.5	Diisopropyl ether	6.9	Diethylamine	8.0
Difluorodichloromethane	5.5	Diethyl ether	7.4	<i>n</i> -Amylamine	8.7
Neopentane	6.3	Isoamyl acetate	7.8	2-Ethylhexanol	9.5
Nitro- <i>n</i> -octane	7.0	Diisobutyl ketone	7.8	Isoamyl alcohol	10.0
<i>n</i> -Pentane	7.0	Di- <i>n</i> -propyl ether	7.8	Acetic acid	10.1
<i>n</i> -Octane	7.6	Sec-butyl acetate	8.2	<i>m</i> -Cresol	10.2
Turpentine	8.1	Isopropyl acetate	8.4	Aniline	10.3
Cyclohexane	8.2	Methyl amyl ketone	8.5	<i>n</i> -Octyl alcohol	10.3
Cymene	8.2	Ethyl acetate	9.0	<i>t</i> -Butyl alcohol	10.9
Carbon tetrachloride	8.6	Methyl ethyl ketone	9.3	<i>n</i> -Amyl alcohol	10.9
<i>n</i> -Propylbenzene	8.6	Butyl cellosolve	9.5	<i>n</i> -Butyl alcohol	11.4
<i>p</i> -Chlorotoluene	8.8	Methyl acetate	9.6	Isopropyl alcohol	11.5
Decalin	8.8	Dichloroethyl ether	9.8	Diethylene glycol	12.1
Xylene	8.8	Acetone	9.9	Furfuryl alcohol	12.5
Benzene	9.2	Dioxane	10.0	Ethanol	12.7
Styrene	9.3	Cyclopentanone	10.4	<i>N</i> -Ethylformamide	13.9
Tetraline	9.4	Cellosolve	10.5	Methanol	14.5
Chlorobenzene	9.5	<i>N,N</i> -Dimethylacetamide	10.8	Ethylene glycol	14.6
Ethylene dichloride	9.8	1,2-Propylene carbonate	13.3	Glycerol	16.5
<i>p</i> -Dichlorobenzene	10.0	Ethylene carbonate	14.7	Water	23.4
Nitroethane	11.1				
Acetonitrile	11.9				
Nitroethane	12.7				

TABLE 3.2 Approximate Solubility Parameter Values for Polymers

Polymer	Poor H Bonding	Moderate H Bonding	Strong H Bonding
Polytetrafluoroethylene	5.8–6.4		
Poly(vinyl ethyl ether)	7.0–11.0	7.4–10.8	9.5–14.0
Poly(butyl acrylate)	7.0–12.5	7.4–11.5	
Poly(butyl methacrylate)	7.4–11.0	7.4–10.0	9.5–11.2
Polyisobutylene	7.5–8.0		
Polyethylene	7.7–8.2		
Poly(vinyl butyl ether)	7.8–10.6	7.5–10.0	9.5–11.2
Natural rubber	8.1–8.5		
Polystyrene	8.5–10.6	9.1–9.4	
Poly(vinyl acetate)	8.5–9.5		
Poly(vinyl chloride)	8.5–11.0	7.8–10.5	
Buna N	8.7–9.3		
Poly(methyl methacrylate)	8.9–12.7	8.5–13.3	
Poly(ethylene oxide)	8.9–12.7	8.5–14.5	9.5–14.5
Poly(ethylene sulfide)	9.0–10.0		
Polycarbonate	9.5–10.0	9.5–10.6	
Poly(ethylene terephthalate)	9.5–10.8	9.3–9.9	
Polyurethane	9.8–10.3		
Polymethacrylonitrile		10.6–11.0	
Cellulose acetate	11.1–12.5	10.0–14.5	
Nitrocellulose	11.1–12.5	8.0–14.5	12.5–14.5
Polyacrylonitrile		12.0–14.0	
Poly(vinyl alcohol)			12.0–13.0
Nylon 66			13.5–15.0
Cellulose			14.5–16.5

parameter can also be determined by adding a nonsolvent to a polymer solution and noting the amount of nonsolvent needed to begin to precipitate the polymers.

Since polar forces are present in polar solvents and polar molecules, this must be considered when estimating solubilities with such *nonregular* solvents and polymers. Hydrogen bonding is also important for some solvents and polymers and again will influence the solubility parameters. Thus, special solubility values have been developed for such solvents (Tables 3.1 and 3.2).

Plasticizers help the flexibility of polymers and are chosen so that they do not dissolve the polymer but rather allow segmental mobility to occur. (In actuality, plasticizers can be considered to *dissolve* small groups of *mers* within the polymer chain.) Through experience, it is found that the solubility parameter differences between the plasticizer and polymer should be less than 1.8 H.

3.3 AVERAGE MOLECULAR WEIGHT VALUES

Small molecules, such as benzene and glucose, have precise structures such that each molecule of benzene has six carbon atoms and six hydrogen atoms. By comparison, each molecule of poly-1,4-phenylene may have a differing number of benzene-derived units, while single molecules (single chains) of PE may vary in the number of ethylene units, the extent and frequency of branching, the distribution of branching, and the length of branching. A few polymers, such as nucleic acids and many proteins, consist of molecules, individual polymer chains that must not vary, so they have a precise molecular weight. The concept of averaging in chemistry is not new. The atomic weights that appear in the periodic table are averages dependent on the natural abundances of various isotopes. In a similar way, the molecular weights of polymeric materials that contain chains of varying chain lengths is also an average dependent on the abundance of the various chain lengths present in the mixture.

While there are several statistically described averages dependent on how we calculate the final average molecular weight from the chain lengths of the individual molecules within the polymer sample, we will concentrate on the two that are most germane to polymers: number-average and weight-average molecular weights. These are averages based on statistical approaches that can be described mathematically and which correspond to physical measurements of specific values.

The number-average value, corresponding to a measure of chain length average, is called the *number-average molecular weight*, \overline{M}_n . Physically, the number-average molecular weight can be measured using any technique that *counts* the molecules, that is, is directly dependent on the number of chains. These techniques include vapor phase and membrane osmometry, freezing point lowering, boiling point elevation, and end-group analysis.

We can describe the number average using a jar filled with plastic capsules such as those used to contain tiny prizes (Figure 3.5a). Here, each capsule contains one polymer chain. All of the capsules are the same size, regardless of the size of the polymer chain. Capsules are then withdrawn, opened, and the individual chain length measured and recorded. A graph such as shown in Figure 3.5b can be constructed from the data with the maximum value being the number-average molecular weight. The probability of drawing a particular capsule is dependent on the *number* of each capsule and not on the size of the chain within the capsule.

The *weight-average molecular weight*, \overline{M}_w , is similarly described, except that the capsule size corresponds to the relative size of polymer chain contained within it (Figure 3.6a). In this approach, the probability of drawing out a particular chain length is dependent on the *size* of the capsule as well as the number of capsules of that size. Larger chains have a greater probability (at least in this exercise) of being drawn out because they are larger and are contained within larger capsules. Again, a graph is constructed and the maximum value is the weight-average molecular weight (Figure 3.6b).

For this exercise we assume that the numbers of chains of a given size are the same in the two jars (Figures 3.5 and 3.6). Compare Figure 3.5b with Figure 3.6b. Notice that the maximum occurs at a higher molecular weight for the weight-average situation. The area of the curve should be the same and the \overline{M}_i ordinate is longer reflecting the extension to a greater molecular weight for the weight-average situation.

Several mathematical moments (about a mean) can be described using the differential or frequency distribution curve, and these can be described by equations. The first moment is the number-average molecular weight, \overline{M}_n . Any measurement that leads to the number of molecules, functional groups, end groups, or particles that are present in a given weight of sample allows the calculation of \overline{M}_n . The \overline{M}_n is calculated like any other numerical average by dividing the sum of the individual molecular weight values by the number of molecules. Thus, \overline{M}_n for three molecules

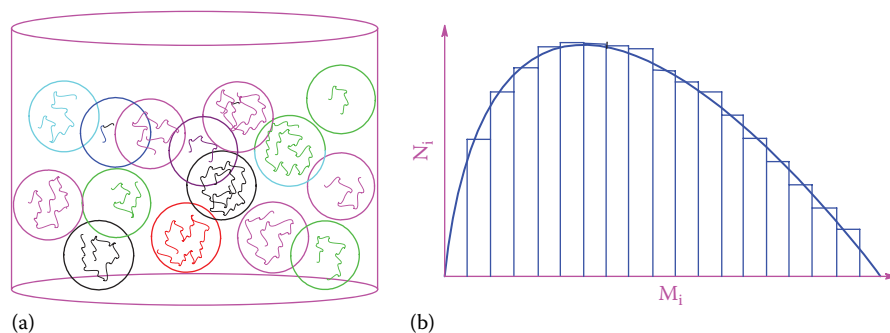


FIGURE 3.5 (a) Jar with capsules, each capsule containing a single polymer chain where the capsule size is the same and independent of the chain size, illustrating the number-average dependence on molecular weight. (b) Molecular weight distribution for a polydisperse polymer sample constructed from *capsule-derived* data for the number-average situation derived from the capsules (a).

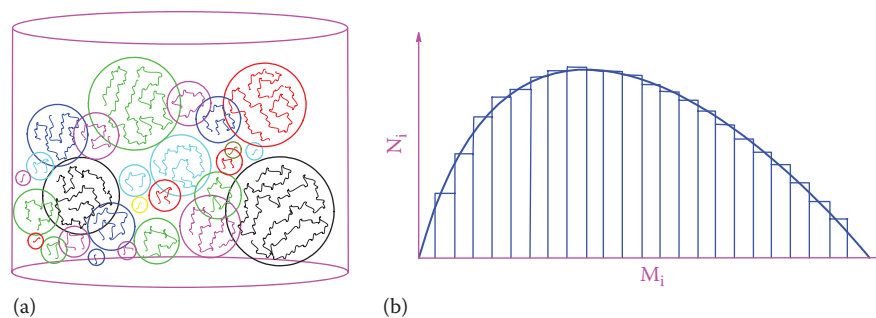


FIGURE 3.6 (a) Jar with capsules, each containing a single polymer chain where the capsule size is directly related to the size of the polymer chain within the capsule. (b) Molecular weight distribution for a polydisperse polymer sample constructed from *capsule-derived* data for the weight-average situation shown in (a).

having molecular weights of 1.00×10^5 , 2.00×10^5 , and 3.00×10^5 is $(6.00 \times 10^5)/3 = 2.00 \times 10^5$. Recalling that $W = \sum W_i = \sum M_i N_i$, the general solution is shown mathematically as

$$(3.4) \quad \bar{M}_n = \frac{\text{Total weight of sample}}{\text{Number of molecules of } N_i} = \frac{W}{\sum N_i} = \frac{\sum M_i N_i}{\sum N_i}$$

Most thermodynamic properties are related to the number of particles present and thus are dependent on \bar{M}_n .

Colligative properties are dependent on the number of particles present and are thus related to \bar{M}_n . \bar{M}_n values are independent of molecular size and are highly sensitive to small molecules present in the mixture. Values of \bar{M}_n are determined by Raoult's techniques that are dependent on colligative properties. These techniques include ebulliometry (boiling point elevation), cryometry (freezing point depression), osmometry, and end-group analysis.

Weight-average molecular weight, \bar{M}_w , is determined from experiments in which each molecule or chain makes a contribution to the measured result relative to its size. This average is more dependent on the number of longer chains than is the number-average molecular weight, which is dependent simply on the total number of each chain.

The \bar{M}_w is the second moment average and is shown mathematically as

$$(3.5) \quad \bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

Thus, the \bar{M}_w of the three chains cited before is

$$\frac{(1.00 \times 10^{10}) + (4.00 \times 10^{10}) + (9.00 \times 10^{10})}{(6.00 \times 10^5)} = 2.33 \times 10^5$$

Bulk properties associated with large deformations, such as viscosity and toughness, are most closely associated with \bar{M}_w . \bar{M}_w values are most often determined by light-scattering photometry.

However, melt elasticity is more closely related to the third moment known as the z-average molecular weight, \bar{M}_z . The \bar{M}_z is most often determined using either light-scattering photometry or ultracentrifugation. It is shown mathematically as

$$(3.6) \quad \bar{M}_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i}$$

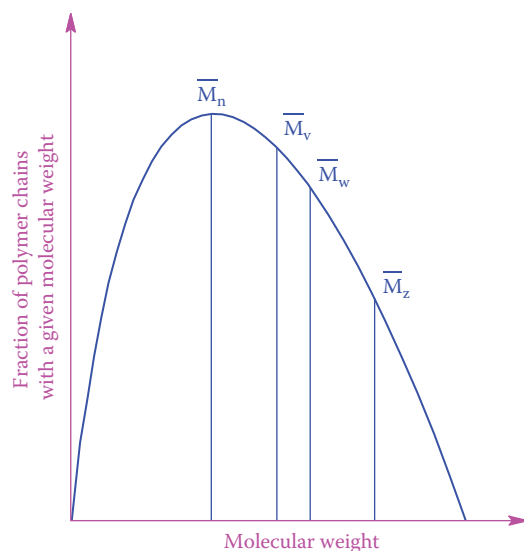


FIGURE 3.7 Molecular weight distributions.

The \bar{M}_z value for the average of the three polymer chains described before is 2.57×10^5 :

$$\frac{(1 \times 10^{15}) + (8 \times 10^{15}) + (27 \times 10^{15})}{[(1 \times 10^{10}) + (4 \times 10^{10}) + (9 \times 10^{10})]} = 2.57 \times 10^5$$

While $Z + 1$ and higher average molecular weight values can be calculated, the major interests are in \bar{M}_n , \bar{M}_v , \bar{M}_w , and \bar{M}_z , which is the order of increasing size for a heterodisperse polymer sample as shown in Figure 3.7. Thus, for heterogeneous molecular weight systems, $\bar{M}_z > \bar{M}_w > \bar{M}_n$. The ratio of \bar{M}_w/\bar{M}_n is called the **polydispersity index**. The most probable polydispersity index for polymers produced by the condensation technique with respect to molecular weight is 2. As the heterogeneity decreases, the various molecular weight values converge until $\bar{M}_z = \bar{M}_w = \bar{M}_n$.

Typical techniques for determining molecular weight are given in Table 3.3. The most popular techniques will be considered briefly. All classical molecular weight techniques require dilute solutions, generally 0.01 g/mL or 1% (1 g/100 mL) solutions. To further minimize solute interactions, extrapolation of the measurements to infinite dilution is normal practice.

For polydisperse polymer samples, measurements that lead directly to the determination of the molecular weight, such as light-scattering photometry and membrane osmometry, are referred to as “absolute molecular weight” methods. Techniques such as viscometry are not absolute molecular weight methods because they require calibration using an absolute molecular weight technique and more about the viscosity average molecular weight in Section 3.9.

3.4 FRACTIONATION OF POLYDISPERSE SYSTEMS

The data plotted in Figure 3.7 were obtained by the fractionation of a polydisperse polymer sample. Polydisperse polymers can be fractionated by a number of techniques. The most widely used technique is chromatography. Other methods include addition of a nonsolvent to a polymer solution, cooling a polymer solution, solvent evaporation, extraction, diffusion, or centrifugation. The molecular weight of the fractions may be determined using any of the classic techniques given in Table 3.3.

TABLE 3.3 Typical Molecular Weight Determination Methods^a

Method	Type of Mol. Wt. Average	Applicable Wt. Range	Other Information
Light scattering	\bar{M}_w	To ∞	Can give other mol. wts. and shape
Membrane osmometry	\bar{M}_n	10^4 – 10^6	
Vapor phase osmometry	\bar{M}_n	To 4×10^4	
Electron and x-ray microscopy	\bar{M}	10^2 to ∞	
Isopiestic method	\bar{M}_n	To 2×10^4	
Ebulliometry (BP elevation)	\bar{M}_n	To 4×10^4	
Cryoscopy (MP depression)	\bar{M}_n	To 5×10^4	
End-group analysis	\bar{M}_n	To 2×10^4	
Osmodialysis	\bar{M}_n	500 – 2.5×10^4	
Centrifugation			
Sedimentation equil.	\bar{M}_z	To ∞	
Archibald mod.	$\bar{M}_{z,w}$	To ∞	
Trautman's method	\bar{M}_w	To ∞	
<i>Sedimentation velocity gives real M for only monodisperse systems</i>			
Chromatography	Calibrated	To ∞	Gives mol. wt. distribution
SAXS	\bar{M}_w		
Mass Spec. MALDI		To 10^7	Mol. wt. distribution
Viscometry	Calibrated		
Coupled Chromatography-LS		To ∞	Mol. wt. distribution, shape, $\bar{M}_{n,w,z}$

^a "To ∞ " means that the molecular weight of the largest particles soluble in a suitable solvent can be, in theory, determined.

3.5 CHROMATOGRAPHY

3.5.1 GENERAL CHROMATOGRAPHY

As noted before, certain techniques such as colligative methods, light-scattering photometry, special MS techniques, and ultracentrifugation allow the calculation of specific or absolute molecular weights. Under certain conditions some of these also allow the calculation of the MWD.

3.5.2 ION-EXCHANGE CHROMATOGRAPHY

There are a wide variety of chromatography techniques including paper and column techniques. Chromatographic techniques involve passing a solution containing the to-be-tested sample through a medium that shows selective absorption for the different components in the solution. *Ion-exchange chromatography* separates molecules on the basis of their electrical charge. Ion-exchange resins are either polyanions or polycations. For a polycation resin, those particles that are least attracted to the resin will flow more rapidly through the column and be emitted from the column first. This technique is most useful for polymers that contain charged moieties.

3.5.3 AFFINITY CHROMATOGRAPHY

In *affinity chromatography*, the resin contains molecules that are especially selected that will interact with the particular polymer(s) that is being studied. Thus, for a particular protein, the resin may be modified to contain a molecule that interacts with that protein type. The solution containing the mixture is passed through the column and the modified resin preferentially

associates with the desired protein allowing it to be preferentially removed from the solution. Later, the protein is washed through the column by addition of a salt solution and collected for further evaluation.

3.5.4 HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

In *high-performance liquid chromatography (HPLC)* Picture 3.1, pressure is applied to the column that causes the solution to rapidly pass through the column allowing procedures to be completed in a fraction of the time in comparison to regular chromatography.

3.5.5 ELECTROPHORESIS

When an electric field is applied to a solution, polymers containing a charge will move either toward the cathode (positively charged species) or toward the anode (negatively charged species). This migration is called *electrophoresis*. The velocity at which molecules move is mainly dependent upon the electric field and change on the polymer driving the molecule toward one of the electrodes and a frictional force dependent on the size and structure of the macromolecule that opposes the movement. In general, the larger and more bulky the macromolecule, the greater the resistance to movement, and the greater the applied field and charge on the molecule, the more rapid the movement. While electrophoresis can be conducted on solutions it is customary to use a supporting medium of a paper or gel. For a given system, it is possible to calibrate the rate of flow with the molecular weight and/or size of the molecule. Here, the flow characteristics of the calibration material must be similar to those of the unknown.

Generally though, electrophoresis is often employed in the separation of complex molecules such as proteins where the primary factor in the separation is the charge on the species. Some amino acids such as aspartic acid and glutamic acid contain an *additional* acid functional group, while amino acids such as lysine, arginine, and histidine contain *additional* basic groups. The presence of these units will confer to the protein tendencies to move toward the anode or cathode. The rate of movement is dependent on a number of factors including the relative abundance and accessibility of these acid and base functional groups.



PICTURE 3.1 HPLC component system.

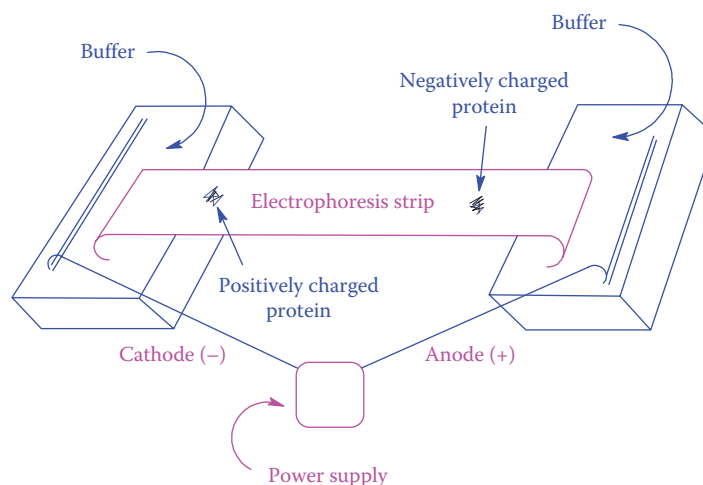


FIGURE 3.8 Basic components of an electrophoresis apparatus.

Figure 3.8 contains an illustration of the basic components of a typical electrophoresis apparatus. The troughs at either end contain an electrolyte buffer solution. The sample to be separated is placed in the approximate center of the electrophoresis strip.

3.5.6 GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC) is a form of chromatography that is based on separation by molecular size rather than chemical properties. GPC or *size exclusion chromatography (SEC)* is widely used for molecular weight and MWD determination. In itself, SEC does not give an absolute molecular weight and must be calibrated against polymer samples whose molecular weight has been determined by a technique that does give an absolute molecular weight.

3.5.7 SIZE EXCLUSION CHROMATOGRAPHY

SEC is an HPLC technique whereby the polymer chains are separated according to differences in hydrodynamic volume. This separation is made possible by the use of special packing material in the column. The packing material is usually polymeric porous spheres often composed of polystyrene cross-linked by addition of varying amounts of divinylbenzene. Retention in the column is mainly governed by the partitioning (or exchanging) of polymer chains between the mobile (or eluent) phase flowing through the column and the stagnate liquid phase that is present in the interior of the packing material.

Through control of the amount of cross-linking, nature of the packing material, and specific processing procedures, spheres of widely varying porosity are available. The motion in and out of the stationary phase is dependent on a number of factors including Brownian motion, chain size, and conformation. The latter two are related to the polymer chain's hydrodynamic volume—the real, excluded volume occupied by the polymer chain. Since smaller chains preferentially permeate the gel particles, the largest chains are eluted first. As noted earlier, the fractions are separated on the basis of size.

The resulting chromatogram is then a molecular size distribution. The relationship between molecular size and molecular weight is dependent on the conformation of the polymer in solution. As long as the polymer conformation remains constant, which is generally the case, molecular size increases with increase in molecular weight. The precise relationship between molecular size and molecular weight is conformation dependent. For random coils, molecular size as measured by the polymer's radius of gyration, R , and molecular weight, M , R is proportional to M^b , where “ b ” is a constant dependent on the solvent, polymer concentration, and temperature. Such values are known and appear in the literature for many polymers allowing the ready conversion of molecular size data collected by SEC into molecular weight and MWD.

There is a wide variety of instrumentation ranging from simple manually operated devices to completely automated systems. Briefly, the polymer-containing solution and solvent alone are introduced into the system and pumped through separate columns at a specific rate. The differences in refractive index between the solvent itself and polymer solution are determined using a differential refractometer. This allows calculation of the amount of polymer present as the solution passes out of the column.

The unautomated procedure was first used to separate protein oligomers using Sephadex gels. Today, there are a wide variety of specialized and general gels used as column packing. The efficiency of these packed columns can be determined by calculating the height in feet equivalent to a theoretical plate, which is the reciprocal of the plate count per feet (P). P is directly proportional to the square of the elution volume (V_e) and inversely proportional to the height of the column in feet and the square of the baseline (D) as follows:

$$(3.7) \quad P = \left(\frac{16}{f} \right) \left[\left(\frac{V_e}{D} \right)^2 \right]$$

Conversion of retention volume for a given column to molecular weight can be accomplished using several approaches including peak position, universal calibration, broad standard, and actual molecular weight determination by coupling the SEC to an instrument that gives absolute molecular weight.

In the *peak position approach*, well-characterized narrow fraction samples of known molecular weight are used to calibrate the column and retention times determined. A plot of log M versus retention is made and used for the determination of samples of unknown molecular weight. Unless properly treated, such molecular weights are subject to error. The best results are obtained when the structures of the samples used in the calibration and those of the test polymers are the same.

The *universal calibration approach* is based on the product of the limiting viscosity number (LVN) and molecular weight being proportional to the hydrodynamic volume. Benoit showed that for different polymers, elution volume plotted against the log LVN times molecular weight gave a common line. In one approach molecular weight is determined by constructing a *universal calibration line* through plotting the product of log LVN for polymer fractions with narrow MWDs as a function of the retention of these standard polymer samples for a given column. Molecular weight is then found from retention time of the polymer sample using the calibration line.

Probably the most accurate approach is to directly connect, couple, the SEC to a device, such as a light-scattering photometer, that directly measures the molecular weight for each elution fraction. Here, both molecular weight and MWD are accurately determined.

3.6 COLLIGATIVE MOLECULAR WEIGHTS

3.6.1 OSMOMETRY

A measure of any of the colligative properties involves counting solute (polymer) molecules in a given amount of solvent. The most common technique for polymers is *membrane osmometry*. The technique is based on the use of a semipermeable membrane through which solvent molecules freely pass, but through which the large polymer molecules are unable to pass. Existing membranes only approximate ideal semipermeability, the chief limitation being the passage of low-molecular-weight chains through the membrane.

There is a thermodynamic drive toward dilution of the polymer-containing solution with a net flow of solvent toward the cell containing the polymer. This results in an increase in liquid in that cell causing a rise in the liquid level in the corresponding measuring tube. This rise in liquid level is opposed and balanced by a hydrostatic pressure resulting in a difference in the liquid levels of the two measuring tubes. The difference is directly related to the osmotic pressure of the polymer-containing solution. Thus, solvent molecules pass through the semipermeable membrane reaching a *static* equilibrium.

Since osmotic pressure is dependent on the number of particles present, the measurement of this osmotic pressure can be used to determine the M_n of the dissolved polymer. The difference

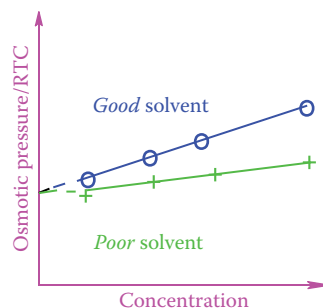


FIGURE 3.9 Plots of osmotic pressure, π , divided by RTC used to determine $1/\overline{M}_n$ in osmometry.

in height (Δh) of the liquids in the columns is converted to osmotic pressure (π) by multiplying the gravity (g) and the density of the solution (ρ), that is, $\pi = \Delta h \rho g$. In the old static osmometers, it might take weeks to months for equilibrium to become established allowing excessive passage of polymer chains through the membrane. Today, automated osmometers allow molecular weight measurements to occur in minutes with a minimal of passage of polymer chains through the membrane. The relationship between molecular weight and osmotic pressure is given in the following van't Hoff equation:

$$(3.8) \quad \pi = \frac{RTC}{\overline{M}_n} + BC^2$$

Thus, the reciprocal of \overline{M}_n is the intercept when data for π/RTC versus C are extrapolated to zero concentration (Figure 3.9).

The slope of the lines in Figure 3.9, that is, the virial constant B , is related to the CED. The value for B would be zero at the theta temperature. Since this slope increases as the solvency increases, it is advantageous to use a dilute solution consisting of a polymer and a poor solvent to minimize extrapolation errors.

In the *vapor phase osmometry* technique, drops of solvent and solution are placed in an insulated chamber in proximity to thermistor probes. Since the solvent molecules evaporate more rapidly from the solvent than from the polymer solution, a temperature difference results that is related to the molarity of the polymer (M) can be determined if the heat of vaporization per gram of solvent (λ) is known using the following relationship:

$$(3.9) \quad \Delta T = \frac{RT^2M}{\lambda 100}$$

3.6.2 END-GROUP ANALYSIS

In cases where the end groups are known and their concentration can be determined, knowledge of their abundance allows a determination of \overline{M}_n . The sensitivity of this method decreases and the chain length becomes greater. Some end groups can be determined using spectroscopic techniques and other through titration.

3.6.3 EBULLIOMETRY AND CRYOMETRY

Raoult's law works for small polymers as well as small molecules. Determination of \overline{M}_n for both *ebulliometry* (boiling point elevation) and *cryometry* (freezing point lowering) is based on the Clausius–Clapeyron equation:

$$(3.10) \quad \overline{M}_n = \left(\frac{RT^2V}{\Delta H} \right) \left(\frac{C}{\Delta T} \right)_{C \rightarrow 0}$$

By use of sensitive thermocouples and care, molecular weights to about 50,000 Da can be determined.

3.7 LIGHT-SCATTERING PHOTOMETRY

Ever watch a dog or young child chase moonbeams? The illumination of dust particles is an illustration of light scattering, not of reflection. Reflection is the deviation of incident light through one particular angle such that the angle of incidence is equal to the angle of reflection. Scattering is the radiation of light in all direction. Thus, in observing the moonbeam, the dust particle directs a beam toward you regardless of your angle in relation to the scattering particle. The energy scattered per second (scattered flux) is related to the size and shape of the scattering particle and to the scattering angle.

Scattering of light is all about us—the fact that the sky above us appears blue, the clouds white, and the sunset is shades of reds and oranges is a consequence of preferential scattering of light from air molecules, water droplets, and dust particles. This scattered light carries messages about the scattering objects.

The measurement of light scattering is the most widely used technique for the determination of \bar{M}_w . This technique is based on the optical heterogeneity of polymer solutions and was developed by Nobel Laureate Peter Debye in 1944.

Today, modern instruments utilize lasers as the radiation source because they provide a monochromatic, intense, and well-defined light source. Depending upon the size of the scattering object, the intensity of light can be essentially the same or vary greatly with respect to the direction of the oncoming radiation. For small particles the light is scattered equally independent of the angle the observer is to the incoming light. For larger particles, the intensity of scattered light varies with respect to the angle of the observer to the incoming light. For small molecules at low concentrations, this scattering is described in terms of the Rayleigh ratio.

In 1871, Rayleigh showed that induced oscillatory dipoles were developed when light passed through gases and that the amount (intensity) of scattered light (τ) was inversely proportional to the fourth power of the wavelength of light. This investigation was extended to liquids by Einstein and Smoluchowski in 1908. These oscillations reradiate the light energy—producing turbidity, that is, the Tyndall effect. Other sources of energy, such as x-rays or laser beams, may be used in place of visible light sources.

For light-scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I_0 , as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light as follows:

$$(3.11) \quad \frac{I}{I_0} = e^{-\tau}$$

where τ is the measure of the decrease of the incident beam intensity per unit length (l) of a given solution and is called the turbidity of the solution.

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solution and of the solvent (n_0), to the molecular weight of the polymer (\bar{M}_w), and to the inverse fourth power of the wavelength of light used (λ). Thus,

$$(3.12) \quad \frac{Hc}{\tau} = \frac{1}{\bar{M}_w P_0} (1 + 2Bc + Cc^2 + \dots)$$

where the expression for the constant H is as follows:

$$(3.13) \quad H = \left[\frac{32\pi^2}{3} \right] \left[\frac{n_0^2 (dn/dc)^2}{\lambda^4 N} \right] \quad \text{and} \quad \tau = K'n^2 \left(\frac{i_{90}}{i_0} \right)$$

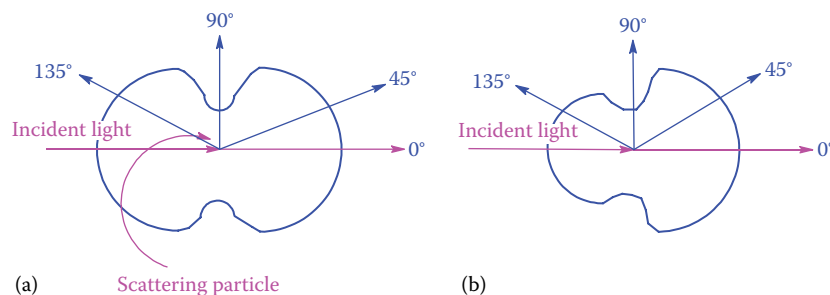


FIGURE 3.10 Light-scattering envelopes. Distance for the scattering particle to the boundaries of the envelope represents an equal magnitude of scattered light as a function of angle for a small scattering particle (a) and a large scattering particle (b).

where

n_0 is the index of refraction of the solvent

n is the index of refraction of the solution

c is the polymer concentration; the virial constants B , C , etc., are related to the interaction of the solvent

P_θ is the particle scattering factor

K' is a constant

N is Avogadro's number

The expression dn/dc is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration

In the determination of \bar{M}_w , one measures the intensity of scattered light at different concentrations and at different angles (θ). The incident light sends out a scattering envelope that has four equal quadrants (Figure 3.10a) for small particles. The ratio of scattering at 45° compared with that for 135° is called the *dissymmetry factor* or *dissymmetry ratio* Z . The reduced dissymmetry factor Z_0 is the intercept of the plot of Z as a function of concentration extrapolated to zero concentration.

For polymer solutions containing polymers of moderate to low molecular weight, P_θ is 1, and Equation 3.14 reduces to 3.18, an equation for a straight line ($y = b + mx$):

$$(3.14) \quad \frac{Hc}{\tau} = \frac{1}{\bar{M}_w} (1 + 2Bc + Cc^2 + \dots)$$

Several expressions are generally used in describing the relationship between values measured by light-scattering photometry and molecular weight. One is given in Equation 3.12 and others, such as Equation 3.15, are analogous except that constants have been rearranged:

$$(3.15) \quad \frac{Kc}{R} = \frac{1}{\bar{M}_w} (1 + 2Bc + Cc^2 + \dots)$$

where $K = [2\pi^2 n^2 / N\lambda^4] [dn/dc]^2$.

At low polymer concentrations, Equation 3.12 reduces to Equation 3.16, which is an equation of a straight line ($y = b + mx$):

$$(3.16) \quad \frac{Hc}{\tau} = \frac{1}{\bar{M}_w} + \frac{2Bc}{\bar{M}_w}$$

When the ratio of the concentration c to the turbidity τ (tau; related to the intensity of scattering at 0° and 90°) multiplied by the constant H is plotted against concentration (Figure 3.11), the intercept of the extrapolated line is the reciprocal of \bar{M}_w and the slope contains the virial constant B . Z_0 is directly related to the particle scattering factor, and both are related to both the size and shape of the scattering particle. As the size of the scattering particle, the individual polymer chain, approaches about one-twentieth the wavelength of the incident light, scattering interference

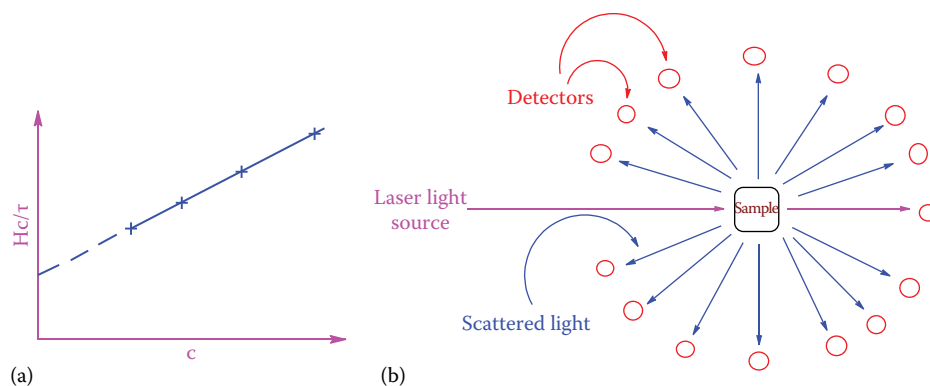


FIGURE 3.11 (a) Typical simple plot used to determine $1/\bar{M}_w$ from scattering data. (b) Multiple detector arrangement showing a sample surrounded by an array of detectors.

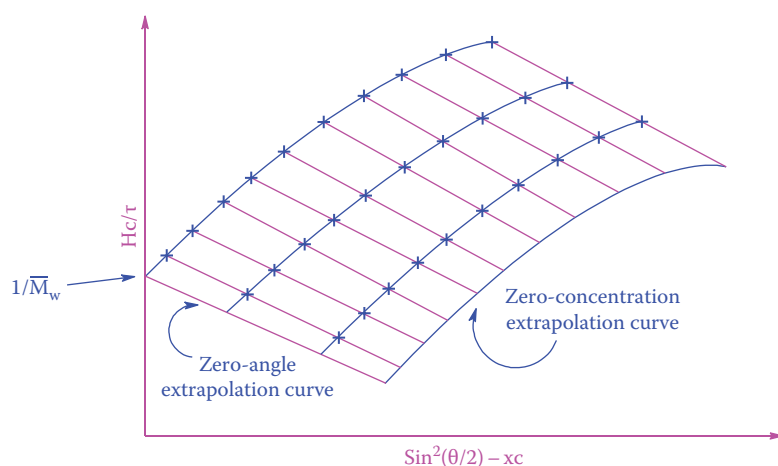


FIGURE 3.12 Zimm plot for a polymer scaled with a negative concentration coefficient (x) to improve data aesthetics and accessibility.

occurs giving a scattering envelope that is no longer symmetrical (Figure 3.10b). Here, the scattering dependency on molecular weight reverts back to the relationship given in Equation 3.12.

The molecular weight for dilute polymer solutions is typically found using one of two techniques. The first technique is called the dissymmetrical method or approach because it utilizes the determination of Z_0 as a function of the particle scattering factor as a function of polymer shape. \bar{M}_w is determined from the intercept through substitution of the determined particle scattering factor. The weakness in this approach is the necessity of having to assume a shape for the polymer in a particular solution. For small Z_0 values, choosing an incorrect polymer shape results in a small error, but for larger Z_0 values, the error becomes significant.

The second approach uses multiple detectors (Figure 3.11) allowing a double extrapolation to zero concentration and zero angle with the data forming what is called a *Zimm plot* (Figure 3.12). The extrapolation to zero angle corrects for finite particle size effects. The radius of gyration, related to polymer shape and size, can also be determined from this plot. The second extrapolation to zero concentration corrects for concentration factors. The intercepts of both plots are equal to $1/\bar{M}_w$.

The Zimm plot approach does not require knowing or having to assume a particular shape for the polymer in solution.

Related to the Zimm plot is the Debye plot. In the Zimm approach, different concentrations of the polymer solution are used. In the Debye approach, one low concentration sample is used with $1/\bar{M}_w$ plotted against $\sin^2(\theta/2)$, essentially one-half of the Zimm plot.

Low-angle laser light-scattering photometry (LALLS) and *multiangle low-angle laser light-scattering photometry (MALS)* take advantage of the fact that at low or small angles, the

scattering particle factor becomes one reducing Equation 3.12 to Equation 3.14 and at low concentrations to Equation 3.16.

A number of automated systems exist with varying capabilities. Some internally carry out dilutions and refractive index measurements allowing molecular weight to be directly determined without additional sample treatment. The correct determination of dn/dc is very important since any error in its determination is magnified because it appears as the squared value in the expression relating light scattering and molecular weight.

Low-angle and multiangle light-scattering photometers are available that allow not only the determination of \overline{M}_w but also additional values under appropriate conditions. For instance, a Zimm plot as shown in Figure 3.12 allows both \overline{M}_w and \overline{M}_n to be determined as well as the mean radius independent of the molecular conformation and branching.

These systems may also allow the determination of molecular conformation matching the radius and molecular weight to graphs showing the change in the root-mean-square radius of gyration and molecular weight for different shaped molecules (Figure 3.13). The expression for the mean square radius of gyration is given as

$$(3.17) \quad r_g^2 = \frac{\sum r_i^2 m_i}{\sum m_i}$$

One of the most important advances in polymer molecular weight determination is the *coupling* of SEC and light-scattering photometry, specifically LALLS or MALS. As noted in Section 3.5, SEC allows the determination of the MWD. In its usual operational configuration, it does not itself allow the calculation of an absolute molecular weight but relies on calibration with polymers of known molecular weight. By coupling HPLC and light-scattering photometry, the molecular weight of each fraction can be determined giving an MWD and various molecular weight values (\overline{M}_w , \overline{M}_z , \overline{M}_n).

The LALLS or MALS detector measures τ -related values, a differential refractive index detector is used to measure concentration, and the SEC supplies samples containing *fractionated* polymer solutions allowing both molecular weight and MWD to be determined. Further, polymer shape can be determined. This combination represents the most powerful, based on ease of operation, variety of samples readily used, cost, means to determine polymer size, shape, and MWD available today.

A general assembly for a SEC-MALS instrument is given in Figure 3.14. A typical three-dimensional plot obtained from such an assembly is shown in Figure 3.15.

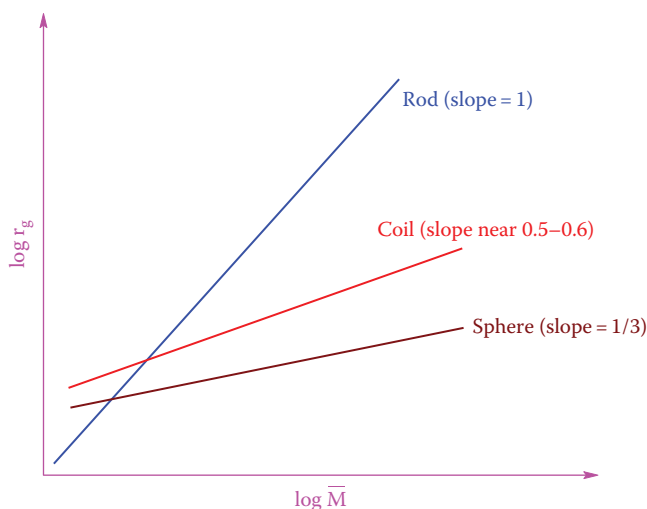


FIGURE 3.13 Standard plot of the log of the mean radius of gyration versus log molecular weight for different shaped macromolecules. Essentially for instance, for a sphere the radius is proportional to the root-mean-square (rms) radius and $\overline{M}^{1/3}$ with a slope in the $\log r_g$ versus $\log \overline{M}$ of 1/3; for rod-shaped polymers, length is proportional to rms radius and \overline{M} with a slope of 1; and for random coils the end-to-end distance is proportional to the rms radius and $\overline{M}^{1/2}$ with a slope of about 0.5–0.6.

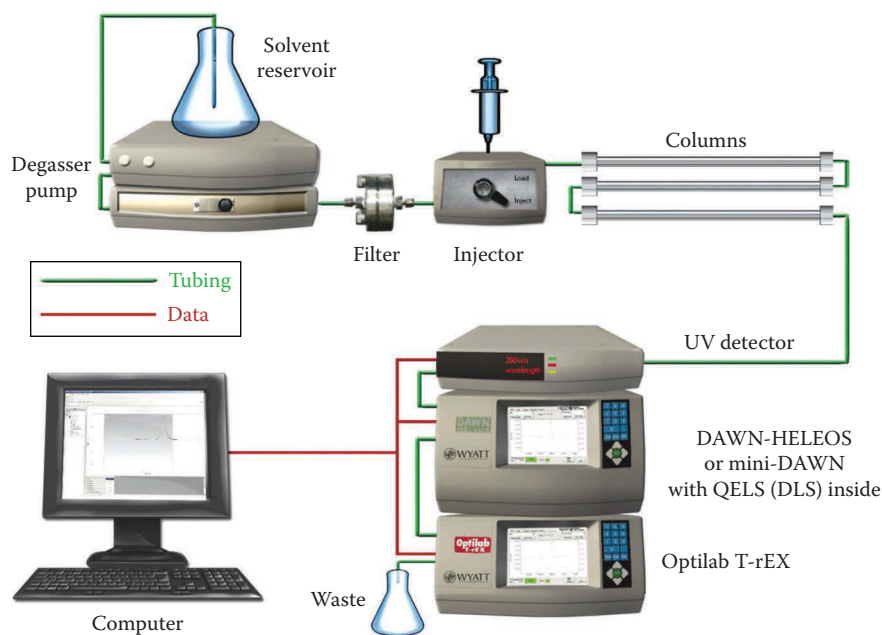


FIGURE 3.14 Typical SEC-MALS setup including refractive index refractometer. (Used with permission of Wyatt Technology Corporation, Santa Barbara, CA.)

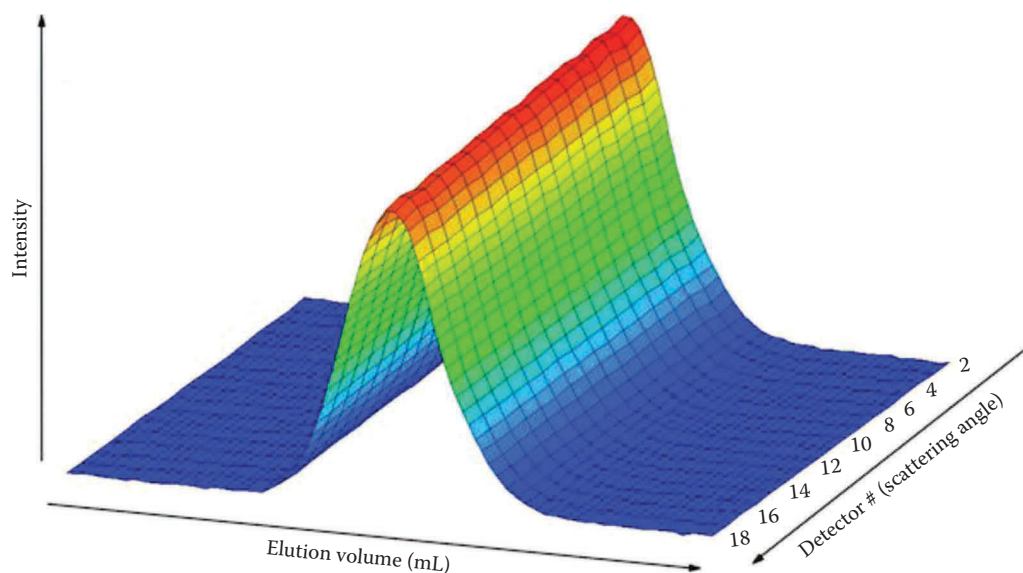


FIGURE 3.15 Three-dimensional plot of scattering intensity as a function of scattering angle and elution volume for a broad molecular weight distribution polystyrene sample (NIST standard reference 706). (Used with permission of Wyatt Technology Corporation, Santa Barbara, CA.)

Dynamic light scattering is similar in principle to typical light scattering. When several particles are hit by oncoming laser light, a spotted pattern appears, the spots originating from the interference between the scattered light from each particle giving a collection of dark (from destructive interference) and light (from constructive interference) spots. This pattern of spots varies with time because of the Brownian motion of the individual scattering particles. The rate of change in the pattern of spots is dependent on a number of features including particle size. The larger the particle, the slower the Brownian motion and consequently the slower the change in the pattern. Measurement of these intensity fluctuations with time allows the calculation of the translational diffusion constant of the scattering particles. The technique for making these

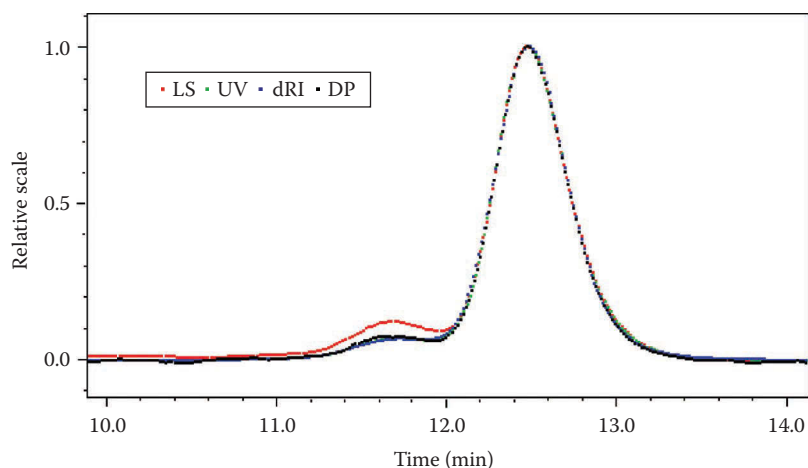


FIGURE 3.16 Response to selected detectors as a function of retention volume for bovine serum albumin sample (dissolved in PBS buffer at a pH of 6.8). The four detectors are the UV (green), dRI (blue) = refractive index signal, LS (red) = light-scattering signal, and DP (black) = differential pressure transducer (viscosity signal). (Used with permission of Wyatt Technology Corporation, Santa Barbara, CA.)

measurements is given several names including dynamic light scattering (DLS) emphasizing the fact that it is the difference in the scattered light with time that is being measured, photon correlation spectroscopy with the name emphasizing the particular mathematical technique employed to analyze the light-scattering data, and quasielastic light scattering with name emphasizing the fact that no energy is lost in the collision between the particle and the light photon.

The effect of subtle particle changes as a function of temperature, sample preparation, time, solvent, and other changes can be measured using DLS. Such changes can then be related to performance variations eventually interrelating structure shape and biological/physical property.

Another variation that is useful employing coupled light scattering is referred to as a *triple detection set*. The set consists of three detectors: a light-scattering detector, a differential refractometer detector, and a capillary differential viscometer. It functions in concert with a GPC and light-scattering source. The GPC separates the polymer mixture into molecular weight fractions. According to the Einstein equation, the intrinsic viscosity times the molecular weight is equal to the hydrodynamic volume or size of polymers in solution. Thus, the molecular weight is determined using light-scattering photometry, viscometry gives the intrinsic viscosity, and the equation is solved for size.

Generally, light-scattering photometry has a limit to determining molecular size with the lower limit being about 10 nm. The addition of the viscometer allows molecular sizes to be determined for oligomeric materials to about 1 nm. The assembly allows an independent measure of size and molecular weight as well as additional conformational and aggregation information including small conformational changes. The assembly also allows good molecular determination to occur even when there are small dn/dc values, low-molecular-weight fractions, absorbing and fluorescent polymers, copolymers with varying dn/dc values, and chiral polymers that depolarize the incident beam.

Figure 3.16 contains data on bovine serum albumin sample obtained using a quadruple detection setup. A molecular weight of 66,000 g/mol is found with a viscosity of 0.0418 dL/g and from this a hydrodynamic radius of 3.50 nm which is essentially the same as the Stokes value of 3.5 nm reported for bovine serum albumin.

3.8 OTHER TECHNIQUES

3.8.1 ULTRACENTRIFUGATION

Since the kinetic energy of solvent molecules is greater than the sedimentation force of gravity, polymer molecules remain suspended in solution. However, this gravitational field, which permits Brownian motion, may be overcome by increasing this force by use of high

centrifugal forces, such as the ultracentrifugal forces created by equipment developed by Nobel Laureate The Svedberg in 1925.

Both \overline{M}_w and \overline{M}_z may be determined by subjecting dilute polymer solutions to high centrifugal forces. Solvents with densities and indices of refraction different from the polymers are chosen to ensure polymer motion and optical detection of this motion. In sedimentation velocity experiments, the ultracentrifuge is operated at extremely high rotational speeds up to over 70,000 rpm in order to transport the denser polymer molecules through the less dense solvent to the cell bottom or to the top if the density of the solvent is greater than the density of the polymer. The boundary movement during ultracentrifugation can be followed using optical measurement to monitor the sharp change in refractive index (n) between the solvent and solution.

The sedimentation velocity determination is dynamic and can be completed in a short period of time. The sedimentation equilibrium method gives quantitative results, but longer time is required for centrifugation at relatively low velocities to establish equilibrium between sedimentation and diffusion.

3.8.2 MASS SPECTROMETRY

Certain mass spectral (MS) procedures allow the determination of the molecular weight or molecular mass of oligomeric to polymeric materials (Table 3.4).

In *matrix-assisted laser desorption/ionization mass spectroscopy (MALDI MS)*, Picture 3.2, the polymer is dissolved, along with a *matrix chemical*, and the solution deposited onto a

TABLE 3.4 Mass Spectrometry Approaches Used in the Determination of Molecular Weights of Oligomeric and Polymeric Materials

MS Type	(Typical) Upper Molecular Weight Range (Da)
(Usual) Electron impact (EI)	To 2000
Fast atom bombardment (FAB)	To 2000
Direct laser desorption (direct LD)	To 10^4
Matrix-assisted laser desorption/ionization (MALDI)	To 10^7



PICTURE 3.2 MALDI MS.

sample probe. The solution is dried. MALDI MS depends on the sample having a strong UV absorption at the wavelength of the laser employed. This helps minimize fragmentation since it is the matrix UV-absorbing material that absorbs most of the laser energy. Often employed UV-matrix materials are 2,5-dihydroxybenzoic acid, sinapinic acid, picolinic acids, and alpha-cyano-4-hydroxycinnamic acid. The high energy of the laser allows both the matrix material and the test sample to be volatilized. Such techniques are referred to as “soft” since the test sample is not subjected to (much) ionizing radiation, and hence, little fragmentation occurs. Mass accuracy on the order of a few parts per million is obtained. Thus, chain content can be determined for copolymers and other chains with unlike repeat units. Polymer MWDs can also be determined using MALDI MS and related MS techniques.

MALDI MS was developed for the analysis of nonvolatile samples and was heralded as an exciting new MS technique for the identification of materials with special use in the identification of polymers. It has fulfilled this promise to only a limited extent. While it has become a well-used and essential tool for biochemists in exploring mainly nucleic acids and proteins, it has been only sparsely employed by synthetic polymer chemists. This is because of the lack of congruency between the requirements of MALDI MS and most synthetic polymers. MALDI MS requires that the test material, polymer, be soluble in a relatively volatile solvent. Proteins, nucleic acids, and PEGs are water soluble, allowing the use of MALDI MS for analysis of their chain length. Most polymers are not readily soluble in such solvents so MALDI MS is of little use in the analysis of these materials. Carraher and coworkers have developed an approach that is applicable to most materials that focuses on analyzing the fragmentation of the polymers. While this technique is not able to give molecular weights and MWDs, it allows the identification of ion fragments and ion fragment clusters up to several thousand daltons.

Recently, MS combinations have been available including the TG-MS combination developed by Carraher that allows the continuous characterization of evolved materials as a polymer undergoes controlled thermal degradation.

3.9 VISCOMETRY

3.9.1 SOLUTION VISCOSITY

Viscosity is a measure of the resistance to flow of a material, mixture, or solution. (The topic of polymer rheology is related to polymer viscosity and is covered in Chapter 13.) Here, we will consider the viscosity of solutions containing small, generally 1 g/100 cm³ (or 1 g/100 mL; called 1% solutions) and less, amounts of polymer. The study of such dilute polymer solutions allows a determination of a *relative* molecular weight. The molecular weight is referred to as “relative” since viscosity measurements have not been directly related, through rigorous mathematical relationships, to a specific molecular weight. By comparison, measurements made using light-scattering photometry and some of the other methods covered before are relatable to specific molecular weight values, and these techniques are said to give us *absolute* molecular weights.

The relationship between the force f necessary to move a plane of area A relative to another plane a distance d from the initial plane (Figure 3.17) is described as

$$(3.18) \quad f \propto \frac{A}{d}$$

In order to make this a direct relationship, a proportionality factor is introduced. This factor is called the *coefficient of shear viscosity* or simply *viscosity*:

$$(3.19) \quad f = \eta \left(\frac{A}{d} \right)$$

Viscosity is then a measure of the resistance of a material to flow. The inverse of viscosity is given the name “*fluidicity*.” As a material’s resistance to flow increases, its viscosity increases. Viscosities have been reported using a number of different names. The CGS unit of viscosity is

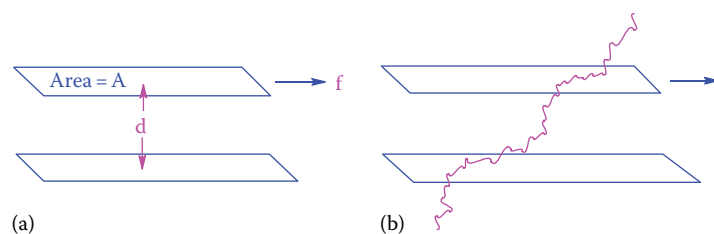


FIGURE 3.17 (a) Representation of Equation 3.18. The representation of (b) illustrates a polymer chain between two flow planes.

TABLE 3.5 Viscosities of Selected Common Materials

Substances	General Viscosity (MPas)
Air	0.00001
Water	0.001
Polymer latexes/paints	0.01
PVC plastisols	0.1
Glycerol	10
Polymer resins and “pancake” syrups	100
Liquid polyurethanes	1,000
Polymer “melts”	10,000
Pitch	100,000,000
Glass	1,000,000,000,000,000,000,000,000

called the poise, which is a dyne seconds per square centimeter. Another widely used unit is the pascal (or Pas), which is Newton seconds per square centimeter. In fact, 1 Pas = 10 poise.

Table 3.5 contains the general magnitude of viscosity for some common materials. It is important to note the wide variety of viscosities of materials from gases such as air to viscoelastic solids as glass.

In polymer science, viscosity is not usually directly measured, but rather relative viscosity is obtained by measuring the flow rate of one material relative to that of a second material. Viscosity is one of the most widely used methods for the characterization of polymer molecular weight because it provides the easiest and most rapid means of obtaining molecular weight–related data that requires minimal instrumentation. A most obvious characteristic of polymer solutions is their high viscosity, even when the amount of added polymer is small. This is because polymers reside in several flow planes (Figure 3.17b) acting to resist the flow of one plane relative to another flow plane.

The ratio of the viscosity of a polymer solution to that of the solvent is called the “**relative viscosity** (η_r).” This value minus 1 is called the “**specific viscosity** (η_{sp}),” and the **reduced viscosity** (η_{red}) or **viscosity number** is obtained by dividing η_{sp} by the polymer concentration c , that is, η_{sp}/c . The **intrinsic viscosity**, or **LVN**, is obtained by extrapolating η_{sp}/c to zero polymer concentration. These relationships are given in Table 3.6, and a typical plot of η_{sp}/c and $\ln \eta_r/c$ is given in Figure 3.18.

TABLE 3.6 Commonly Used Viscosity Terms

Common Name	Recommended Name (IUPAC)	Definition	Symbol
Relative viscosity	Viscosity ratio	η/η_0	$\eta_{rel} = \eta_r$
Specific viscosity	—	$(\eta/\eta_0) - 1$ or $(\eta - \eta_0)/\eta_0$	η_{sp}
Reduced viscosity	Viscosity number	η_{sp}/c	η_{red} Or η_{sp}/c
Inherent viscosity	Logarithmic viscosity number	$(\ln \eta_r)/c$	η_{inh} Or $(\ln \eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	Limit $(\eta_{sp}/c)_{c \rightarrow 0}$ Or limit $((\ln \eta_r)/c)_{c \rightarrow 0}$	LVN

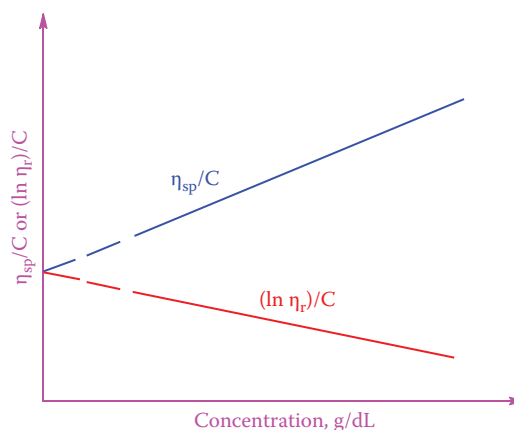


FIGURE 3.18 Reduced and inherent viscosity-concentration lines for a dilute polymer solution.

Staudinger showed that the intrinsic viscosity of a solution ($[\eta]$) or LVN is related to the molecular weight of the polymer. The present form of this relationship was developed by Mark–Houwink (and is known as the “[Mark–Houwink equation](#)”) in which the proportionality constant K is characteristic of the polymer and solvent and the exponential “ a ” is a function of the shape of the polymer in a solution. For theta solvents, the value of “ a ” is 0.5. This value, which is actually a measure of the interaction of the solvent and polymer, increases as the coil expands and the value is between 1.8 and 2.0 for rigid polymer chains extended to their full contour length and 0 for spheres. When a is 1.0, the Mark–Houwink equation (3.20) becomes the Staudinger viscosity equation:

$$(3.20) \quad \text{LVN} = K\bar{M}^a$$

Values of “ a ” and “ K ” have been determined and compiled in several polymer handbooks and are dispersed throughout the literature. With known a and K values, molecular weight can be calculated using Equation 3.20. As noted before, viscosity is unable to give absolute molecular weight values and must be calibrated, that is, values of a and K are determined using polymer samples where their molecular weights have been determined using some absolute molecular weight method such as light-scattering photometry. It is customary in determining the a and K values to make a plot of $\log \text{LVN}$ versus $\log \bar{M}$ since the log of Equation 3.20, that is, Equation 3.21, is a straight line relationship where the slope is a and intercept K . In reality, a is determined from the slope but K is determined by simply selecting a known $\text{LVN}-\bar{M}$ couple and using the determined a value to calculate the K value:

$$(3.21) \quad \log \text{LVN} = a \log \bar{M} + \log K$$

The intrinsic viscosity or LVN, like melt viscosity, is temperature dependent and decreases as temperature increases as shown in the following equation:

$$(3.22) \quad \text{LVN} = A e^{E/RT}$$

However, if the original temperature is below the theta temperature, the viscosity will increase when the mixture of polymer and solvent is heated to a temperature slightly above the theta temperature.

Viscosity measurements of dilute polymer solutions are carried out using a viscometer, such as either of those pictured in Figure 3.19. The viscometer is placed in a constant temperature bath and the time taken for a polymer solution to flow through a set space in the viscometer measured.

In Equation 3.20 “ a ” values for random coils range from 0.5 for theta solvents to 0.8 for good solvents, 0 for hard spheres, about 1 for semicoils, and 2 for rigid rods.

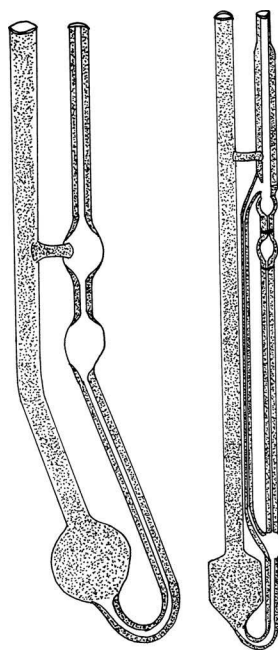


FIGURE 3.19 Common solution viscometers.

For linear polymers at their theta temperature, that is, the temperature where the chain attains unperturbed dimensions, the Flory equation resembles the Mark–Houwink equation where α is equal to 1.0 as shown in the following equation:

$$(3.23) \quad [\eta] = K \overline{M}^{1/2} \alpha^3 = K' \overline{M}^{1/2}$$

The intrinsic viscosity of a solution, like the melt viscosity, is temperature dependent and decreases as temperature increases (3.24):

$$(3.24) \quad [\eta] = A e^{E/RT}$$

While the description of viscosity is complex, the relative viscosity is directly related to the flow-through times using the same viscometer as shown in Equation 3.25 where t and t_0 are the flow times for the polymer solution and solvent, respectively, and the density of the solution (ρ) and solvent (ρ_0) are related as in the following equation:

$$(3.25) \quad \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0} = \eta_r$$

Since the densities of the dilute solution and solvent are almost the same, they are normally cancelled giving the following equation:

$$(3.26) \quad \frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r$$

Thus, the relative viscosity is simply a ratio of flow times for the polymer solution and solvent. Reduced viscosity is related to the LVN by a virial equation:

$$(3.27) \quad \frac{\eta_{sp}}{c} = [\eta] + k_1 [\eta]^2 c + k' [\eta]^3 c^2 + \dots$$

For most dilute solutions, Equation 3.33 reduces to the *Huggins viscosity relationship* (Equation 3.28):

$$(3.28) \quad \frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c$$

which allows $[\eta]$ to be determined from the intercept of the plot of η_{sp}/c versus c and is the basis for the top plot given in Figure 3.18.

Another relationship often used in determining $[\eta]$ is called the inherent viscosity equation and is given in the following equation:

$$(3.29) \quad (\ln \eta_r)/c = [\eta] - k_2[\eta]^2 c$$

Again, a plot of $(\ln \eta_r)/c$ versus c gives a straight line with the intercept $[\eta]$ (or LVN) after extrapolation to zero polymer concentration. This is the basis of the lower plot in Figure 3.18. While k_1 and k_2 are mathematically found to give the following relationship,

$$(3.30) \quad k_1 + k_2 = 0.5$$

many systems appear not to follow this relationship.

3.9.2 MELTED POLYMER VISCOSITIES

We will now turn our attention from the viscosity of dilute solutions and look at the viscosity of melted polymers. The viscosity of melted polymers is important when resins are transferred and in polymer processing when determining the correct conditions to have a specific flow rate for injection processing and in determining the optimum conditions to get the necessary dimensions of extruded shapes. Fillers, plasticizers, temperature, solvents, and molecular weight are just some of the variables that influence the viscosity of polymer melts. Here, we will look at the dependence of melt viscosity on polymer molecular weight. Polymer melts have viscosities on the order of 10,000 MPas (1 centipoise is equal to 0.001 Pas/s).

For largely linear polymers, such as linear polystyrene, where there are not present particularly bulky side chains, the viscosity or flow is mainly dependent on the chain length. In most polymers the melt viscosity–chain length relationship has two distinct regions where the region division occurs when the chain length reaches some length called the “critical entanglement chain length (Z)” where intermolecular entanglement occurs. This intermolecular entanglement causes the individual chains in the melt to act as being much more massive because of the entanglement. Thus, the resistance to flow is a combination of the friction and entanglement between chains as they slide past one another. Below the critical entanglement length, where only the friction part is important, the melt viscosity, η , is related to the weight-average molecular weight by

$$(3.31) \quad \eta = K_l \bar{M}_w^{1.0}$$

And above the critical chain length, where both the friction and entanglement are important, the relationship is

$$(3.32) \quad \eta = K_h \bar{M}_w^{3.4}$$

where

K_l is a constant for the precritical entanglement chain length

K_h is for the situation above Z and where both K values are temperature dependent

The first power dependence is due to the simple increase in molecular weight as chain length increases, but the 3.4 power relationship is due to a complex relationship between chain movement as related to entanglement and diffusion and chain length.

TABLE 3.7 Viscosity Measuring Techniques and Their Usual Range

Technique	Typical Range (Poises)
Capillary pipette	0.01–1,000
Falling sphere	1–100,000
Parallel plate	10,000– 10^9
Falling coaxial cylinder	100,000– 10^{11}
Stress relaxation	1,000– 10^{10}
Rotating cylinder	1– 10^{12}
Tensile creep	100,000–greater than 10^{12}

The critical chain length often corresponds to the onset of *strength*-related properties and is often considered the lower end for useful mechanical properties. The Z value for polymers varies but is generally between about 200 and 1000 units in length. For instance, the Z value for polystyrene is about 700; for polyisobutylene about 600; for poly(decamethylene sebacate) about 300; for poly(methyl methacrylate) about 200; and for poly(dimethyl siloxane) about 1000.

A number of techniques have been developed to measure melt viscosity. Some of these are listed in Table 3.7. Rotational viscometers are of varied structures. The Couette cup and bob viscometer consists of a stationary inner cylinder, the bob, and an outer cylinder, cup, that is rotated. Shear stress is measured in terms of the required torque needed to achieve a fixed rotation rate for a specific radius differential between the radius of the bob and cup. The Brookfield viscometer is a bob and cup viscometer. The Mooney viscometer, often used in the rubber industry, measures the torque needed to revolve a rotor at a specified rate. In the cone and plate assemblies, the melt is sheared between a flat plate and a broad cone whose apex contacts the plate containing the melt.

A number of capillary viscometers or rheometers have been employed to measure melt viscosity. In some sense these operate on a principle similar to the simple observation of a trapped bubble moving from the bottom of a shampoo bottle when it is turned upside down. The more viscous the shampoo, the longer it takes for the bubble to move through the shampoo.

SUMMARY

1. Some naturally occurring polymers such as certain proteins and nucleic acids consist of molecules with a specific molecular weight and are called monodisperse. However, many other natural polymers, such as cellulose and natural rubber, and most synthetic polymers consist of molecules with different molecular weights and are called polydisperse. Many properties of polymers are dependent on their chain length. Since the melt viscosity increases exponentially with chain length, the high energy costs of processing high-molecular-weight polymers are not often justified.
2. The distribution of chain lengths in a polydisperse system may be represented on a typical probability-like curve. The \bar{M}_n is the smallest in magnitude of the typically obtained molecular weights and is a simple arithmetic mean that can be determined using any technique based on colligative properties, such as osmotic pressure, boiling point elevation, freezing point depression, and end-group determination. \bar{M}_w is larger than \bar{M}_n and is referred to as the second power relationship for disperse polymer chains. This value is most often determined by light-scattering photometry. Light-scattering photometry and the colligative-related values are referred to as absolute molecular weight values because there is a direct mathematical connection between molecular weight and the particular property used to determine molecular weight.
3. For monodisperse samples, $\bar{M}_n = \bar{M}_w$. For polydisperse samples the ratio of \bar{M}_w/\bar{M}_n is a measure of the polydispersity and is given the name polydispersity index. The viscosity molecular weight must be calibrated using samples whose molecular weight has been determined using an absolute molecular weight determination technique, thus it is not an absolute molecular weight determining technique, but it requires simple equipment,

- and is easy to measure. The Mark–Houwink relationship, $LVN = KM^a$, is used to relate molecular weight and viscosity.
4. The number-average molecular weight is dependent on the number of polymer chains, while the weight-average molecular weight is dependent on the size of the chains. Thus, there is a correlation between the way the molecular weight is obtained and the type of molecular weight obtained.
 5. MWD is most often measured using some form of chromatography. In GPC cross-linked polymers are used in a column and act as a sieve allowing the larger molecules to elute first. After calibration, the molecular weight of the various fractions of the polymer can be determined. Combinations such as chromatography coupled with light-scattering photometry are used to obtain the molecular weight of the various fractions in a continuous manner.
 6. While some techniques such as membrane osmometry and light-scattering photometry give absolute molecular weight, other techniques such as viscometry give only relative molecular weights unless calibrated employing a technique that gives absolute molecular weight. After calibration between viscometry values and chain length through some absolute molecular weight method, viscometry is a fast, inexpensive, and simple method to monitor molecular weight.
 7. In general, polymers are soluble in less solvents and to a lower concentration than similar smaller molecules. This is because entropy is the driving force for solubility and smaller molecules have larger entropy values when solubility is achieved in comparison to polymers. Polymers also take longer to dissolve since it takes time for the solvent molecules to penetrate the polymer matrix.
 8. Flory and Huggins developed an interaction parameter that may be used as a measure of the solvent power of solvents for amorphous polymers. Flory and Krigbaum introduced the idea of a theta temperature, which is the temperature at which an infinitely long polymer chain exists as a statistical coil in a solvent.
 9. Hildebrand developed solubility parameters to predict the solubility of nonpolar polymers in nonpolar solvents. The solubility parameter is the square root of the CED. For polar solvents, special solvent–polymer interactions can be incorporated into the solubility parameter approach.

GLOSSARY

Affinity chromatography: Chromatography in which the resin is designed to contain moieties that interact with particular molecules and/or units within a polymer chain.

Bingham plastic: Plastic that does not flow until the external stress exceeds a critical threshold value.

Brownian motion: Movement of larger molecules in a liquid that results from a bombardment of smaller molecules.

Buoyancy factor: In ultracentrifugation experiments, it determines the direction of polymer transport under the effect of centrifugal forces in the cell.

Chromatography: Family of separation techniques based on the use of a medium that shows selective absorption.

Colligative properties: Properties of a solution that are dependent on the number of solute molecules present.

Cloud point: Temperature at which a polymer starts to precipitate when the temperature is lowered.

Cohesive energy density (CED): Heat of vaporization per unit volume.

Commercial polymer range: Molecular weight range high enough to have good physical properties but not too high for economical processing.

Cryometry: Measurement of number-average molecular weight from freezing point depression.

Ebulliometry: Measurement of number-average molecular weight from boiling point elevation.

Effective hydrodynamic volume: Cube of the root-mean-square end-to-end distance of a polymer chain.

Electrophoresis: Form of chromatography that uses an electric field to separate molecules.

End-group analysis: Determination of number-average molecular weight by determination of end groups.

Flory–Huggins theory: Theory used to predict the equilibrium behavior between liquid phases containing polymer.

Fractional precipitation: Fractionation of polydisperse systems by addition of small amounts of nonsolvent to a solution of polymer.

Fractionation of polymers: Separation of a polydisperse polymer into fractions of similar molecular weight.

Gel permeation chromatography: Type of liquid–solid elution chromatography that separates solutions of polydisperse polymer solutions into fractions containing more homogeneous chain sizes by means of a sieving action of a swollen cross-linked polymeric gel. Also called SEC.

High-performance liquid chromatography (HPLC): Chromatography in which pressure is applied that causes the solution to pass more rapidly through the column.

Hildebrand (H): Unit used for solubility parameter values.

Ion-exchange chromatography: Chromatography that separates molecules on the basis of their electrical charge employing polyanionic or polycationic resins.

Kauri-Butanol values: Measure of the aromaticity of a solvent.

Low-angle laser light-scattering photometry (LALLS): Light scattering that employs low-angle measurements minimizing the effect of polymer shape on the scattering.

Mark–Houwink equation: Relates limiting viscosity number to molecular weight; $LVN = KM^a$.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS): Mass spectrometry in which the sample is placed in a matrix that contains a strong UV absorber chosen to match the UV absorption of the laser that allows the molecules to become volatilized with minimal fragmentation.

Melt index: Measure of the flow related inversely to melt viscosity.

Monodisperse: System containing molecules of only one chain length.

Multiangle low-angle laser light-scattering photometry (MALS): Similar to LALLS except where the necessary angle ratios are made together; employs low-angle measurements minimizing the effect of polymer shape on the scattered light.

Number-average molecular weight: Arithmetical mean value obtained by dividing the sum of the molecular weights by the number of molecules.

Oligomer: Polymers with 2–10 repeat units. *Oligos* means *few*.

Osmometry: Gives number-average molecular weight from osmotic pressure measurements.

Polydisperse: Mixture of polymer chains of different lengths.

Raoult's law: States that the vapor pressure of a solvent in equilibrium with a solution is equal to the product of the mole fraction of the solvent and the vapor pressure of the pure solvent. This relationship is used in obtaining number-average molecular weights.

SEC-MALS and SEC-LALLS: Coupled chromatography and light-scattering photometry that allows the determination of a number of important values along with chain length distribution.

Sedimentation equilibrium experiment: Ultracentrifugation technique that allows chain length information to be determined.

Semipermeable membrane: Membrane that permits the diffusion of solvent molecules but not large molecules.

Size exclusion chromatography (SEC): Chromatography in which separation is by molecular size or differences in hydrodynamic volume; also called gel permeation chromatography (GPC); can use the universal calibration approach to obtain molecular weight.

Solubility parameter: A numerical value equal to the square root of the CED, which is used to predict polymer solubility.

Theta solvent: Solvent in which the polymer chain exists as a statistical coil.

Theta temperature: Temperature at which a polymer of infinite molecular weight begins to precipitate.

Ultracentrifuge: Centrifuge that increases the force of gravity by as much as 100,000 times causing a distribution of materials in a solution to separate in accordance with chain length.

Vapor pressure osmometry: Technique for determining the number-average molecular weight by measuring the relative heats of evaporation of a solvent from a solution and pure solvent.

Viscosity: Resistance to flow.

Intrinsic viscosity: The limiting viscosity number obtained by extrapolation of the reduced viscosity to zero concentration.

Reduced viscosity: Specific viscosity divided by the polymer concentration.

Relative viscosity: Ratio of the viscosities of a solution and its solvent.

Specific viscosity: Difference between the relative viscosity and 1.

Weight-average molecular weight: Second power average of molecular weight; dependent on the size of the particular chains.

Zimm plot: Type of double extrapolation used to determine the weight-average molecular weight in light-scattering photometry.

EXERCISES

- Which of the following is polydisperse with respect to chain length: (a) casein, (b) commercial polystyrene, (c) paraffin wax, (d) cellulose, or (e) *Hevea brasiliensis*?
- If the number-average molecular weight for LDPE is 1.4 million, what is the corresponding average chain length?
- What are the number and weight-average molecular weights for a mixture of five molecules each having the following molecular weights: 1.25×10^6 , 1.35×10^6 , 1.5×10^6 , 1.75×10^6 , and 2.00×10^6 ?
- What is the most probable value for the polydispersity index for (a) a monodisperse polymer and (b) a polydisperse polymer synthesized by a condensation technique?
- List in increasing values: \overline{M}_z , \overline{M}_n , \overline{M}_w , and \overline{M}_v .
- Which of the following provides an absolute measure of the molecular weight of polymers: (a) viscometry, (b) cryometry, (c) osmometry, (d) light-scattering photometry, or (e) GPC?
- What is the relationship between the intrinsic viscosity or limiting viscosity number and average molecular weight?
- What molecular weight determination techniques can be used to fractionate polydisperse polymers?
- Which of the following techniques yields a number-average molecular weight: (a) viscometry, (b) light-scattering photometry, (c) ultracentrifugation, (d) osmometry, (e) ebulliometry, or (f) cryometry?
- What kind of molecular weight do you generally get from light-scattering photometry?
- What is the value of the exponent a in the Mark–Houwink equation for polymers in theta solvents?
- How many amino groups are present in each molecule of nylon 66 made from an excess of hexamethylenediamine?
- What is the value of the exponent in the Mark–Houwink equation for a rigid rod?
- If the values of K and a in the Mark–Houwink equation are $1 \times 10^{-2} \text{ cm}^3/\text{g}$ and 0.5, respectively, what is the average molecular weight of a polymer whose solution has an intrinsic viscosity of $150 \text{ cm}^3/\text{g}$?
- Which polymer of ethylene will have the highest molecular weight: (a) a trimer, (b) an oligomer, or (c) a UHMWPE?
- What is a Zimm plot?
- What type of molecular weight average, \overline{M}_n or \overline{M}_w , is based on colligative properties?
- What principle is used in the determination of molecular weight by vapor pressure osmometry?
- Why does the melt viscosity increase faster with molecular weight increase than other properties such as tensile strength?
- In spite of the high cost of processing, UHMPE is used for making trash cans and other durable goods. Why?
- Under what conditions are the weight- and number-average molecular weight the same?
- What is the driving force for polymer solubility?

23. What are colligative methods for measuring molecular weight and what kind of molecular weight do you get?
24. What is the advantage of using viscometry to measure molecular weight?
25. Which will yield the higher apparent molecular weight values in the light-scattering method: (a) a dust-free system or (b) one in which dust particles are present?
26. Does HPLC need to be calibrated before it can give absolute molecular weights?
27. Which of the following does modern LC allow: the calculation of (a) weight-average molecular weight, (b) radius of gyration, (c) number-average molecular weight, (d) MWD, or (e) polydispersity index?
28. What is the significance of the virial constant B in osmometry and light-scattering equations?
29. According to Hildebrand, what is a regular solvent?
30. Which of the two steps that occur in the solution process can be accelerated by (a) agitation (b) swelling or (c) dispersion of the polymer particles?
31. Define CED.
32. For solution to occur, the change in Gibbs free energy must be (a) 0, (b) <0 , or (c) >0 .
33. Will a polymer swollen by a solvent have higher or lower entropy than the solid polymer?
34. Define the change in entropy in the Gibbs free energy equation.
35. Is a liquid that has a value of 0.3 for its interaction parameter a good or a poor solvent?
36. What is the value of the Gibbs free energy change at the theta temperature?
37. What term is used to describe the temperature at which a polymer of infinite molecular weight precipitates from a dilute solution?
38. At which temperature will the polymer coil be larger in a poor solvent: (a) at the theta temperature, (b) below the theta temperature, or (c) above the theta temperature?
39. If the solubility parameter for water is 23.4 H, what is the CED for water?
40. What is the heat of mixing of two solvents having identical solubility parameters?
41. If the density of a polymer is 0.85 g/cm³ and the molar volume is 1,176,470 cm³, what is the molecular weight?
42. Name some steps that generally occur when a polymer is dissolved.
43. Why is it important to determine polymer chain length?
44. Why do δ values decrease as the molecular weight increases in a homologous series of aliphatic polar solvents?
45. Which would be a better solvent for polystyrene: (a) *n*-pentane, (b) benzene, or (c) acetonitrile?
46. Which will have the higher or greater slope when its reduced viscosity or viscosity number is plotted against concentration: a solution of polystyrene (a) in benzene or (b) in nonane?
47. What are general typical values for a in the viscosity relationship to molecular weight?
48. When is the Flory Equation similar to the Mark–Houwink equation?
49. What is the term used for the cube root of the hydrodynamic volume?
50. Explain why the viscosity of a polymer solution decreases as the temperature increases.
51. Is MALDI MS restricted to use for natural polymers such as proteins and nucleic acids.
52. Which of the following would you expect to be most soluble in water: ethanol, hexane, or benzene? Why?
53. If entropy is the driving force for mixing and solubility, why is there such a focus on enthalpy through the various approaches with solubility parameters and other similar values?
54. If MALDI MS is of such great use to biopolymer chemists, why is it not more widely used by synthetic polymer chemists?

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Naturally Occurring Polymers

One of the most rapidly growing areas of science and polymers involves natural polymers. Our bodies are largely composed of polymers: deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, and polycarbohydrates. The “health” of these polymers is related to aging, awareness, mobility, strength, and so on, that is, all the characteristics of being alive. Many medical, health, and biological advances focus on polymers. There is an increasing emphasis on such natural polymers. The emphasis on the human genome and relationships between genes and proteins, and our health underlies much of this movement. Thus, an understanding of polymeric principles is advantageous to those desiring to pursue a career related to their natural environment, be it medicine, biomedical, biological, bioengineering, etc.

Physically, there is no difference in the behavior, study, or testing of natural and synthetic polymers. The techniques suitable for application to synthetic polymers are equally applicable to the study and behavior of natural polymers.

Proteins and nucleic acids typically act as individual units, the nanoworld in action, while many other natural polymers and synthetic polymers act in concert with one another. This is not entirely true since proteins and nucleic acids, while acting as individual units, act with other essential biologically important units to carry out their tasks. Synthetic polymers generally act as groups of chains through chain entanglement giving the overall aggregate such desired properties as strength. In a real sense, the behavior of branched natural polymers such as amylopectin is similar to the branched low-density polyethylene, while the behavior of linear amylose is similar to that of the largely linear high-density polyethylene.

While the specific chemistry and physics dealing with synthetic polymers is complicated, the chemistry and physics of natural polymers is even more complex because of a number of related factors, including (1) the fact that many natural polymers are composed of different, often similar but not identical, repeat units; (2) a greater dependency on the exact natural polymer environment; (3) the question of real structure of many natural polymers in their natural environment is still not well known for many natural polymers; and (4) the fact that polymer shape and size are even more important and complex in most natural polymers than in synthetic polymers.

Industrially, we are undergoing a reemergence of the use of natural polymers as feedstocks and materials in many old and new areas. Since natural polymers are typically regeneratable or renewable resources, nature continues to synthesize them as we harvest them. Many natural polymers are available in large quantities. For instance, cellulose makes up about one-third of the bulk of the entire vegetable kingdom, being present in corn stocks, tree leaves, grass, and so on. With the realization that we must conserve and regulate our chemical resources comes the awareness that we must find substitutes for resources that are not self-renewing, thus, the reason for the increased emphasis in polymer chemistry toward the use and modification of natural, renewable polymers by industry.

Natural feedstocks must serve many human purposes. Carbohydrates as raw materials are valuable due to their actual or potential value. For example, commercial plants are already utilizing rapidly reproducing reengineered bacteria that metabolize cellulose wastes converting it to more protein-rich bacteria that is harvested and then used as a protein source feed meal for animals. Further, natural materials can be used themselves in applications now reserved largely for only synthetic polymers. There is available sufficient natural materials to supply both food and polymer needs.

When plant or animal tissues are extracted with nonpolar solvents, a portion of the material dissolves. The components of this soluble fraction are called lipids and include fatty acids, triacylglycerols, waxes, terpenes, prostaglandins, and steroids. The insoluble portion contains the more polar plant components including carbohydrates, lignin, proteins, and nucleic acids.

Many renewable feedstocks are currently summarily destroyed (through leaving them to rot or burning) or utilized in a noneconomical manner. Thus, leaves are “ritualistically” burned each fall. A number of these seemingly useless natural materials have already been utilized as feedstock sources for industrial products with more becoming available.

Biological polymers represent successful strategies that are being studied by scientists as avenues to different and better polymers and polymer structure control. Sample “design rules” and approaches that are emerging include the following:

- Identification of mer sequences that give materials with particular properties
- Identification of mer sequences that cause certain structural changes
- Formation of a broad range of materials with a wide variety of general/specific properties and function (such as proteins/enzymes) through a controlled sequence assembly from a fixed number of feedstock molecules (proteins, about 20 different amino acids; five bases and two sugar units for nucleic acids)
- Integrated, in situ (in cells), polymer productions with precise nanoscale control
- Repetitive use of proven strategies with seemingly minor structural differences but resulting in quite divergent results (protein for skin, hair, and muscle)
- Control of polymerizing conditions that allow steady-state production far from equilibrium

There often occurs a difference in “mind-set” between the nucleic acid and protein biopolymers covered in this chapter and other biopolymers and synthetic polymers covered in this and other chapters. Nucleic acids and proteins are site specific with one conformation. Generally, if it differs in structure or geometry from the specific macromolecule needed, it is discarded. Nucleic acids and proteins are not a statistical average, but rather a specific material with a specific chain length and conformation. By comparison, synthetic and many other biopolymers are statistical averages of chain lengths and conformations. All of these distributions are often kinetic and/or thermodynamic driven.

This difference between the two divisions of biologically important polymers is also reflected in the likelihood that there are two molecules with the exact same structure. For molecules such as polysaccharides and those based on terpene-like structures, the precise structures of individual molecules vary, but for specific proteins and nucleic acids, the structures are identical from molecule to molecule. This can be considered a consequence of the general function of the macromolecule. For polysaccharides, the major, though not the sole function, are energy and structure. For proteins and nucleic acids, main functions include memory and replication, in addition to proteins sometimes also serving a structural function.

Another difference between proteins and nucleic acids and other biopolymers and synthetic polymers involves the influence of stress–strain activities on the material properties. Thus, application of stress on many synthetic polymers and some biopolymers encourages realignment of polymer chains and regions often resulting in a material with greater order and strength. Counter, application of stress to certain biopolymers, such as specific proteins and nucleic acids, causes a decrease in performance (through denaturation, etc.) and strength. For these biopolymers, this is a result of the biopolymer already existing in a compact and “energy-favored” form and already existing in the “appropriate” form for the desired performance. The performance requirements for the two classifications of polymers are different. For one set, including most synthetic and some biopolymers, performance behavior involves response to stress–strain application with respect to certain responses such as chemical resistance, absorption enhancement, and other physical properties. By comparison, the most cited performances for specific nucleic acids and proteins involve selected biological responses requiring specific interactions occurring within a highly structured environment with specific shape and electronic requirements.

Just to bring natural polymers a little closer to home, the following might be our breakfast from the viewpoint of natural polymers:

Milk	Coffee cake
Proteins	Gluten
Fruit	Starches
Starches	Dextrins
Cellulose	Scrambled eggs
Pectin	Ovalbumin
	Conalbumin
	Ovomucoid
	Mucins
	Globins

4.1 POLYSACCHARIDES

Carbohydrates are the most abundant organic compounds, constituting three-fourths of the dry weight of the plant world. They represent a great storehouse of energy as a food for humans and animals (Picture 4.1). About 400 billion tons of sugars are produced annually through photosynthesis, dwarfing the production of other natural polymers, with the exception of lignin. Much of this synthesis occurs in the oceans, pointing to the importance of harnessing this untapped food, energy, and renewable feedstocks storehouse.

The potential complexity of even the simple aldohexose monosaccharides is indicated by the presence of five different chiral centers, giving rise to 2^5 or 32 possible stereoisomeric forms of the basic structure, two of which are glucose and mannose. While these sugars differ in specific biological activity, their gross chemical reactivities are almost identical, permitting one to often employ mixtures within chemical reactions without regard to actual structure. Their physical properties are also almost the same, again allowing for the mixing of these structures with little loss in physical behavior. But their biological properties are markedly different.



PICTURE 4.1 Sources of carbohydrates.

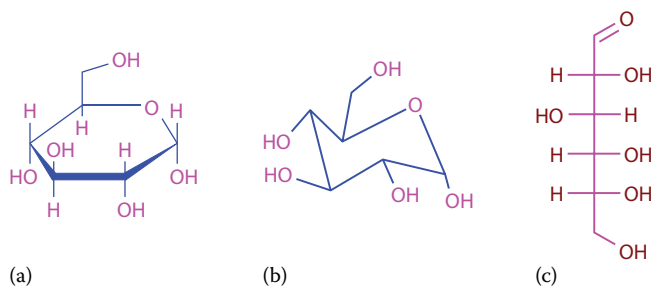
TABLE 4.1 Naturally Occurring Polysaccharides

Polysaccharide	Source	Monomeric Sugar Unit(s)	Structure	Mol. Wt.
Amylopectin	Corn, potatoes	D-Glucose	Branched	10^6 – 10^7
Amylose	Plants	D-Glucose	Linear	10^4 – 10^6
Chitin	Animals	2-Acetamidoglucose		
Glycogen	Animals(muscles)	D-Glucose	Branched	$>10^8$
Inulin	Artichokes	D-Fructose	(Largely) Linear	10^3 – 10^6
Mannan	Yeast	D-Mannose	Linear	—
Cellulose	Plants	D-Glucose	Linear (2D)	10^6
Xylan	Plants	D-Xylose	(Largely) Linear	—
Lichenan	Iceland moss	D-Glucose	Linear	10^5
Galactan	Plants	D-Galactose	Branched	10^4
Arabinoxylan	Cereal grains	L-Arabinofuranose linked to xylose chain	Branched	$>10^4$
Galactomannans	Seed mucilages	D-Mannopyranose chains with D-galactose side chains	(Largely) Linear	10^5
Arabinogalactan	Lupin, soybean, coffee beans	D-Galactopyranose chain, side chain galactose, arabinose	Branched	10^5
Carrageenan	Seaweeds	Complex	Linear	10^5 – 10^6
Agar	Red seaweeds	Complex	Linear	—
Alginate	Brown seaweeds	β -D-Mannuronic acid and α -L-guluronic acid	Linear	—

Carbohydrates are diverse with respect to occurrence and size. Familiar mono- and disaccharides include glucose, fructose, sucrose (table sugar), cellobiose, and mannose. Familiar polysaccharides are listed in Table 4.1 along with their source, purity, and molecular weight range.

The most important polysaccharides are cellulose and starch. These may be hydrolyzed to lower-molecular-weight carbohydrates (oligosaccharides) and finally to D-glucose. Glucose is the building block for many carbohydrate polymers. It is called a monosaccharide since it cannot be further hydrolyzed while retaining the ring. Three major types of representations are used to reflect saccharide structures. These are given in Figure 4.1. Here, we will mainly use the Boeseken–Haworth planer hexagonal rings to represent polysaccharide structures.

Simple sugars exist in both cyclic and linear forms. Intramolecular nucleophilic reactions occur creating equilibrium combinations of these linear and cyclic forms. Monosaccharides are classified according to certain characteristics. Here, we will deal only with the cyclic designations since the polysaccharides are cyclic in nature. The only exception is the nature of the end groups that may be cyclic or linear. For our purposes, these classification characteristics are the stereo placement of the alcohol groups on the ring, the size of the ring, and the placement of the ether linkage. Figure 4.2 contains cyclic representations of glucose that contains six atoms in the ring so it is a hexose. With the exception of carbons 1 and 6, the carbons are stereocenters or stereogenic making D-glucose one of $2^4 = 16$ possible stereoisomers.

**FIGURE 4.1** Alpha-D-glucose using the (a) Boeseken–Haworth, (b) chair, and (c) linear representations.

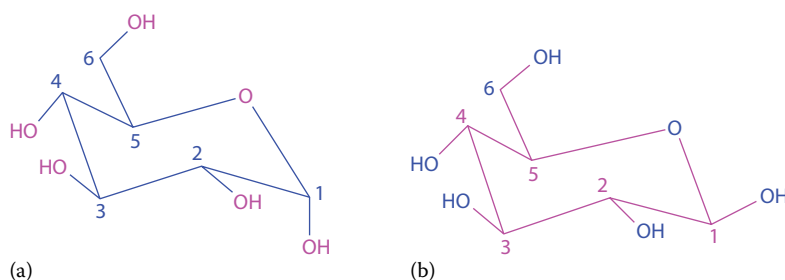


FIGURE 4.2 The α (a) and β (b) anomers of glucose.

Of particular importance is the placement of the hydroxyl group at carbon 1 since many of the most important complex or polysaccharides are linked through ether formation at this hydroxyl group. Assuming the bond between carbons 5 and 6 is coming toward you (out of the page), the linkage at carbon 1 is called the α form since it is going away from us or into the page; that is, it is on the opposite side of the bond between carbons 5 and 6, while β is the other form where the hydroxyl at carbon 1 is on the same side as the bond between carbons 5 and 6. In some ways, considering only the placement of carbon 6 relative to the hydroxyl on carbon 1, the α form is *trans*, while the β form is *cis*.

4.2 CELLULOSE

Cellulose was originally “discovered” by Payen in 1838. For thousands of years, impure cellulose formed the basis of much of our fuel and construction systems in the form of wood, lumber (cut wood), and dried plant material and served as the vehicle for the retention and conveying of knowledge and information in the form of paper and clothing in the form of cotton, ramie, and flax. Much of the earliest research was aimed at developing stronger materials with greater resistance to the natural elements (including cleaning) and to improve dyeability so that the color of choice by common people for their clothing material could be other than a drab white. In fact, the dyeing of textile materials, mainly cotton, was a major driving force in the expansion of the chemical industry in the latter part of the nineteenth century.

Cellulose is a polydisperse polymer with an average DP in the general range of 3,500–36,000. Native cellulose is widely distributed in nature and is the principal constituent of cotton, kapok, flax, hemp, jute, ramie, and wood. Cellulose comprises more than one-third of all vegetable matter and is the world’s largest renewable resource. Much cellulose is derived from woody plants as trees, but more is found as grasses and plants (Picture 4.2). Approximately 50 billion tons is produced annually by land plants, which absorb 4×10^{20} cal of solar energy. Natural cotton fibers, which are the seed hairs from *Gossypium*, are about 1–2 cm in length and about 5–20 μm in diameter. The molecules in native cellulose are present in threadlike strands or bundles called fibrils. Cellulose is not found in a pure form but rather it is associated with other materials such as lignin and hemicelluloses. Cotton contains the purest form of cellulose. Wood, in its dry state, contains 40%–55% cellulose, 15%–35% lignin, and 25%–40% hemicellulose. Plant pulp is the major source of commercial cellulose. The extraction of cellulose from plants is called pulping. Pulping is achieved using thermomechanical, chemical, or mechanical approaches. Plant pulp, from wood, is the major source of nontextile fibers while cotton is the major source of textile fibers.

Cellulose in the form of cotton is used in the textile industry in cloths, cartons, carpets, blankets, and sheets. While cotton was once the king of fabrics, it is still the material of choice for two of the most recognized clothing items—the T-shirt (Picture 4.3) and blue jeans (Picture 4.4).



PICTURE 4.2 Cattails present in a mixed media of pen and ink and water color drawn by the author.



PICTURE 4.3 The almost universal cotton T-shirts. (From Shutterstock, <http://www.shutterstock.com/pic.mhtml?id=236850346&src=id>.)



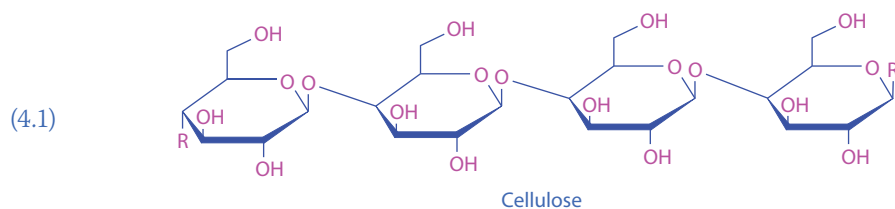
PICTURE 4.4 The ubiquitous cotton blue jeans.

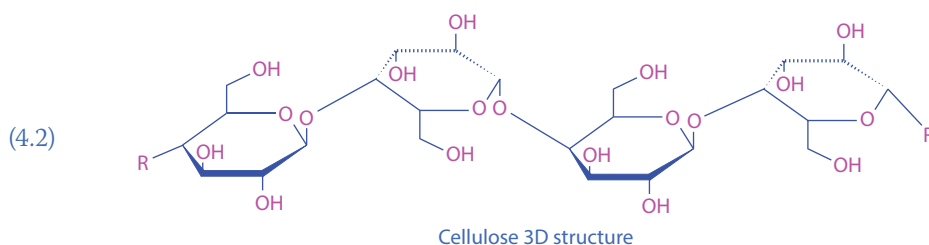
Paper is made from cellulose. Cellulosic fibers are also used as filter materials in artificial kidneys and reverse osmosis though today most kidney dialysis units use cuprammonium tubular films derived from cellulose rather than cellulose itself.

While the celluloses are often largely linear, they are not soluble in water because of the presence of strong intermolecular hydrogen bonding and sometimes the presence of a small amount of cross-linking. Highly ordered crystalline cellulose has a density as high as 1.63 g/cm^3 , while amorphous cellulose has a density as low as 1.47 g/cm^3 . High-molecular-weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide, is called α -cellulose. The fraction that is soluble in 17.5% sodium hydroxide but insoluble in 8% solution is called β -cellulose and what is soluble in 8% sodium hydroxide is called γ -cellulose.

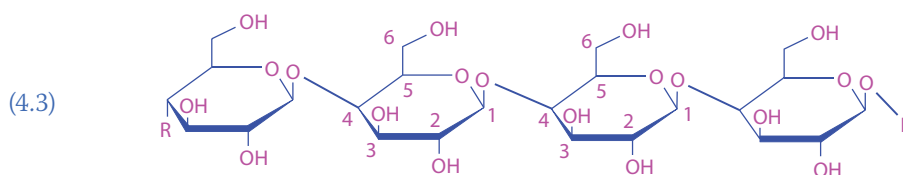
Strong basic solutions, such as sodium hydroxide, penetrate the crystalline lattice of α -cellulose producing an alkoxide called alkali or soda cellulose. Mercerized cotton is produced by aqueous extraction of the sodium hydroxide.

Most linear celluloses may be dissolved in solvents capable of breaking the strong hydrogen bonds. These solutions include aqueous solutions of inorganic acids, calcium thiocyanate, zinc chloride, lithium chloride, ammonium hydroxide, iron sodium tartrate, and cadmium or copper ammonium hydroxide (Schweitzer's reagent). The product precipitated by the addition of a non-solvent to these solutions is highly amorphous regenerated cellulose.





Structure 4.1 is most commonly employed as a description of the repeat unit of cellulose, but the lower structure (4.2) more nearly represents the actual 3D structure with each D-glucosyl unit rotated 180°. We will employ a combination of these two structural representations. The numbering is shown in (4.3) and the type of linkage is written as $1 \rightarrow 4$ since the units are connected through oxygens contained on carbons 1 and 4 as shown here:



We also call the linkage, by agreement with the anomeric nature of the particular carbons involved in linking together the glucosyl units, a beta- or β -linkage. Thus, this linkage is a $\beta 1 \rightarrow 4$ linkage. The other similar $1 \rightarrow 4$ linkage found in starch is called an alpha or α -linkage. The geometric consequence of this difference is great. The linear arrangement of cellulose with the β -linkage gives an arrangement where the OH groups reside somewhat uniformly on the outside of the chain allowing close contact and ready hydrogen bond formation between chains. This arrangement results in a tough, insoluble, rigid, and fibrous material that is well suited as cell wall material for plants. By comparison, the α -linkage of starch (viz., amylose) results in a helical structure where the hydrogen bonding is both interior and exterior to the chain allowing better wettability. This difference in bonding also results in one material being a “meal” for humans (the α -linkage), whereas the other is a meal for termites. The reason for this is the difference in the composition of enzymes present in the two species—humans with the enzyme capability to lyse or break α -linkages and for cows and termites and other species that contain symbiotic bacteria in their digestive systems that furnish the enzymes capable to digest or break the β -glucoside linkages.

While the stomach acid in humans and most animals can degrade polysaccharides to the energy-giving glucose monomeric units, this is not efficient unless there is a specific enzyme, normally present in the gut, which allows the ready and rapid degradation of polysaccharides. Since these enzymes are somewhat specific, their ability to degrade is polysaccharide specific.

The various crystalline modifications have different physical properties and chemical reactivities. These variations are a consequence of the properties varying according to plant source, location in the plant, plant age, season, seasonal conditions, treatment, etc. Thus, in general, bulk properties of polysaccharides are generally measured with average values and tendencies given. These variations are not important for most applications but possibly are important for specific biological applications where the polysaccharide is employed as a drug, within a drug delivery system, or as a biomaterial within the body.

The generation of ethanol from various bacteria using cellulosic materials has occurred for many years. More recently has been the production of ethanol from various enzymes via degradation of cellulose into sugars leading to the ethanol production. The initial step often utilizes glucoamylase enzymes to decompose the cellulose into sugar for eventual fermenting into ethanol. Current efforts involve enlarging the feedstock scope from corn itself to include corncobs and cornstalks and then into leaves, branches, and other cellulosic-intense “waste” materials. Currently, the enzymes are expensive and not particularly efficient. A few years ago, the enzyme

cost was \$6 for every gallon of ethanol produced with the goal of 30 cents for gallon of ethanol produced so that the enzyme cost would not be the limiting factor.

4.2.1 PAPER

It is believed that paper was invented by Ts'ai in China around the second century AD. The original paper was a mixture of bark and hemp. Paper was first produced in the United States by William Rittenhouse in Germantown, PA, in 1690 and this paper was made from rags. Paper was named after the papyrus plant, *Cyperus papyrus*. Trees are the major commercial source of cellulose in the form of wood (Picture 4.5).

Paper comes in many forms with many uses. If you are reading this from a book, then what you are reading from is made from paper; we have paper plates, paper napkins, newspapers and magazines, and cardboard boxes. In fact, the amount of paper items is probably over twice, by weight, which of all the synthetic polymers combined. About 30% paper is writing and printing paper. The rest is mainly used for tissues, toweling, and packaging. If you rip a piece of ordinary paper, not your book page please, you will see that it consists of small fibers. Most of these cellulosic fibers are randomly oriented, but a small percentage are preferentially oriented in one direction because the paper is made from a cellulose-derived watery slurry with the water largely removed through the use of heated rollers that somewhat orient the fibers.

Modern paper is made from wood pulp, largely cellulose, which is obtained by the removal of lignin from debarked wood chips by use of chemical treatments with sodium hydroxide, sodium sulfite, or sodium sulfate. Newsprint and paperboard, which are generally thicker than paper, often contain a greater amount of residual lignin. Paper products can be divided by many different categories such as largely nonprinted materials such as cardboard and sheet paper (Picture 4.6) and highly colored paper such as newsprint, magazines, paper-folded objects as lanterns and



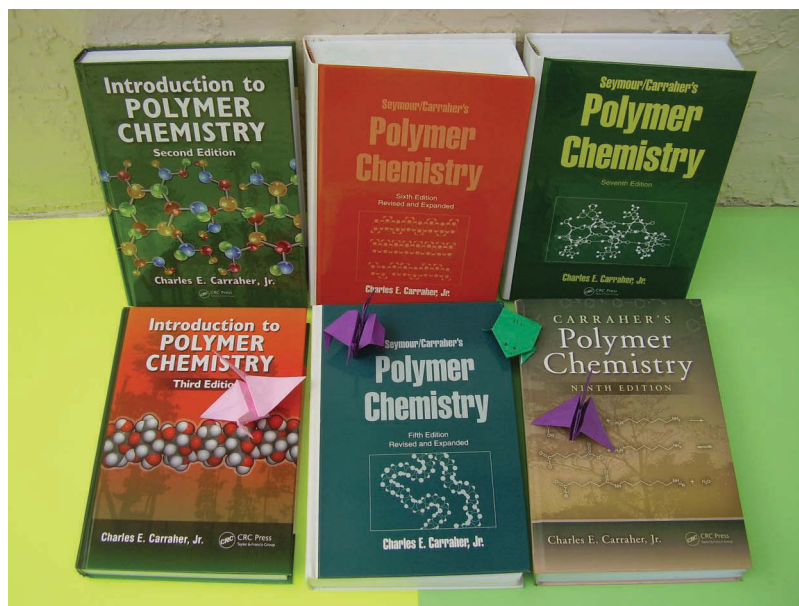
PICTURE 4.5 Trees are the main source of wood. The trees here are slash pines native to South Florida. The trees were currently populated by ibis's.



PICTURE 4.6 Largely unprinted paper goods including poster board, cardboard boxes and cup-holders, and sheet paper in almost any color.

figures, and books and comic books (Picture 4.7). In fact, there is color all about us with most of the color captured by pictures that is expressed on paper.

Wood is almost entirely composed of cellulose and lignin. In the simplest paper-making scheme, the wood is chopped, actually torn, into smaller fibrous particles as it is pressed against a rapidly moving pulp stone. A stream of water washes the fibers away dissolving much of the water-soluble lignin. The insoluble cellulosic fibers are concentrated into a paste called pulp. The pulp is layered into thin sheets and rollers are used to both squeeze out much of the water and assist in achieving paper of uniform thickness. This paper is not very white. It is also not



PICTURE 4.7 Past editions of some of the author's textbooks with paper-folded animals. (Made by John and Timothy Carragher.)

very strong. The remaining lignin is somewhat acidic (lignin contains acidic phenolic groups that hydrolyze to give a weakly acidic aqueous solution) that causes the hydrolytic breakdown of the cellulose. Most of the newsprint is of this type or it is regenerated, reused paper.

Pulping processes are designed to remove the non-saccharide lignin portion of wood that constitutes about 25 of the dry weight. The remaining is mostly cellulose with about 25% hemicellulose (noncellulose cell wall polysaccharides that are easily extracted by dilute aqueous base solutions). Pulping procedures can be generally classified as semichemical, chemical, and semi-mechanical. In semimechanical pulping, the wood is treated with water or sulfate, bisulfite, or bicarbonate solution that softens the lignin. The pulp is then ground or shredded to remove much of the lignin giving purified or enriched cellulose content. The semichemical process is similar, but digestion times are longer and digesting solutions more concentrated giving a product with less lignin but the overall yield of cellulose-intense material is lowered by 70%–80%. Further, some degradation of the cellulose occurs.

Most paper is produced by the chemical process where chemicals are employed to solubilize and remove most of the lignin. While overall yields are lower than the other two main processes, the product gives good quality writing and printing paper. Three main chemical processes are used. In the soda process, extracting solutions containing about 25% sodium hydroxide and 2.4% sodium carbonate are used. In the sulfite process, the extracting solution contains a mixture of calcium dihydrogen sulfite and sulfur dioxide. The sulfide process utilizes sodium hydroxide, sodium monosulfide, and sodium carbonate in the extracting solution.

After the chemical treatment, the pulped wood is removed, washed, and screened. Unbleached, brown-colored paper is made directly from this material. Most whiten or bleached paper is made from treatment of the pulp with chlorine, chlorine dioxide, hypochlorite, and/or alkaline extraction. In general, sulfate pulped paper is darker and requires more bleaching and alkaline extraction to give a “white” pulp.

The *sulfide process*, also called the “kraft” process (the term “kraft” comes from the Swedish word for strong since stronger paper is produced), is more commonly used. The kraft process is favored over the sulfite treatment of the paper because of environmental considerations. The sulfite process employs more chemicals that must be disposed of—particularly mercaptans, RSHs, which are quite odorous. Research continues on reclaiming and recycling pulping chemicals.

If pure cellulose was solely used to make paper, the fiber mat would be somewhat water soluble with only particle surface polar groups and internal hydrogen bonding acting to hold the fibers together. White pigments such as clay and titanium dioxide (titanium IV oxide) are added to help “cement” the fibers together and to fill voids producing a firm, white writing surface. This often occurs as part of an overall coating process.

Most paper is coated to provide added strength and smoothness. The coating is basically an inexpensive paint that contains a pigment and a small amount of polymeric binder. Unlike most painted surfaces, most paper products are manufactured with a short life time in mind with moderate performance requirements. Typical pigments are inexpensive low-refractive index materials such as platelike clay and ground natural calcium carbonate. Titanium dioxide is used only when high opacity is required. The binder may be a starch or latex or a combination of these. The latexes are usually copolymers of styrene, butadiene, acrylic, and vinyl acetate. Other additives and coloring agents may also be added for special performance papers. Resins in the form of surface coating agents and other special surface treatments (such as coating with polypropylene and polyethylene) are used for paper products intended for special uses such as “paper” milk cartons, ice cream cartons, lightweight building materials, and drinking cups. The cellulose supplies the majority of the weight (typically about 90%) and strength with the special additives and coatings providing special properties needed for the intended use.

A better understanding of the nature of paper and films made from synthetic polymers such as polyethylene can be seen when considering why authorities worry about anthrax escaping from a paper envelope yet confining anthrax in a plastic container with no fear of it escaping. When you hold good paper up to the light or tear it you will observe the tiny fibers that compose paper. Even though these fibers appear tiny, they are very large in comparison to individual polymer chains, be they cellulose or polyethylene. The web of chains for cellulose composes eventually the cellulose fibers that are put together physically forming paper with lots of “unoccupied” spaces between the fibers with the spaces of sufficient size to allow the escape of the anthrax.



PICTURE 4.8 Wood in its native form is widely used in building and in the construction of a number of “finer” items including a wide variety of stringed instruments including this viola and bow.

By comparison, polyethylene film has relatively little “unoccupied” space between the individual chains with the entire film composed of these individual chains with no large spaces so that the anthrax cannot escape.

Along with building, native wood is also employed in the construction of many other materials including a wide variety of stringed instruments (Picture 4.8).

4.2.2 PAPER RECYCLING

Recycling of paper continues. Today, up to about one-half of our paper products are recycled and this fraction is increasing as we do a better job of collecting and recycling paper products. Recycling saves both on the natural resource and on energy, water, and other commodities related to paper production.

There exists an interesting dilemma. With the increase in a paperless society, the amount of paper to recycle is decreasing. Yet there is a need for recycled paper. There exists continued research to recover paper attempting to create an endless recycling of the scarce cellulosic fibers with intact cell walls. Virgin pulp from newly harvested trees has long and strong fibers that become shorter and weaker each time they are recycled.

Along with a lessening of recycled paper, there is a consolidation of both paper manufacturers and providers of chemicals related to paper. Along with the decreased virgin paper, the marketplace for a sustainable paper is becoming more difficult.

Paper, including recycled paper, is made by pouring a slurry of water containing about 1% pulp onto a platform of wire mesh. As the water drips through, a damp film of pulp is left behind that is dried giving raw paper. At this point, the paper lacks most of the finer qualities. As noted earlier, the raw paper undergoes a number of additional treatments depending on the amount of recycled pulp in this raw paper and the intended end use. In one treatment developed by Hercules and introduced by Ashland, performance chemicals based on modified polyamines are introduced. The polyamines form both ionic and hydrogen bonds with the paper fibers connecting both the longer and shorter fibers together giving a stronger paper. This stronger paper allows papermakers to run their machines at increased speeds. This allows more paper product to be made for a given time as well as allowing a greater amount of recycled paper to be incorporated into the finished product.

Recycled paper also possesses unwanted microbes, waxes, adhesives, etc. Microbes are typically eliminated using variety of chemicals including bleach, chlorine dioxide, and hypobromous acid. These are all strong oxidizers that are both costly and decompose the cellulosic fibers and present a less than entirely acceptable environment. Alternatives have been introduced including high-energy radiation and other chemicals such as ammonium bromide that act as biocides under milder conditions.

4.3 CELLULOSE-REGENERATING PROCESSES

4.3.1 DISSOLVING AND PRECIPITATION OF CELLULOSE

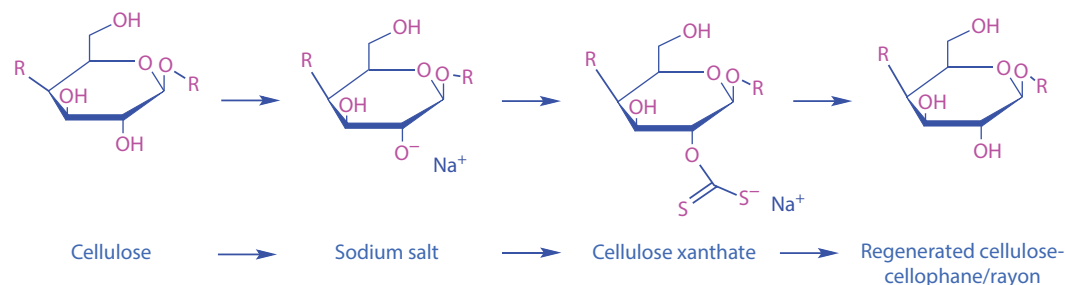
Cellulose is sometimes used in its original or native form as fibers for textile and paper, but often it is modified through dissolving and reprecipitation or through chemical reaction. The *xanthate viscose process*, which is used for the production of rayon and cellophane, is the most widely used regeneration process. The cellulose obtained by the removal of lignin from wood pulp is converted to alkali cellulose. The addition of carbon disulfide to the latter produces cellulose xanthate.

While terminal hydroxyl and aldehyde groups, such as present in cellobiose, are also present in cellulose, they are not significant because they are only present at the ends of very long chains.

The hydroxyl groups are not equivalent. For instance, the pKa values of the two ring hydroxyl groups are about 10 and 12 that is about the same as the hydroxyl groups on hydroquinone and the first value about the same as the hydroxyl on phenol. The pKa value of the nonring or methylene hydroxyl group is about 14 about the same as found for typical aliphatic hydroxyl groups.



In the cellulose regenerating process, sodium hydroxide is initially added such that approximately one hydrogen, believed to be predominately a mixture of the hydroxyl groups on carbons 2 and 3, is replaced by the sodium ion. This is followed by treatment with carbon disulfide forming cellulose xanthate that is eventually recharged back again, regenerated, to cellulose. This sequence is depicted here:



(4.6)



PICTURE 4.9 Women's rayon pants.

The orange-colored xanthate solution, or viscose, is allowed to age and is then extruded as a filament through holes in a spinneret. The filament is converted to cellulose when it is immersed in a solution of sodium bisulfite, zinc II sulfate, and dilute sulfuric acid. The tenacity, or tensile strength, of this regenerated cellulose is increased by a stretching process that reorients the molecules so that the amorphous polymer becomes more crystalline. Cellophane is produced by passing the viscose solution through a slit die into an acid bath. Rayon is used in producing a wide variety of clothing items (Picture 4.9) while cellophane is still employed as a packaging material (Picture 4.10).

Important noncellulosic textile fibers are given in Table 4.2 and a listing of important cellulosic textile fibers is given in Table 4.3.

Since an average of only one hydroxyl group in each repeating glucose unit in cellulose reacts with carbon disulfide, the xanthate product is said to have a degree of substitution (DS) of 1 out of a potential DS of 3.

Partially degraded cellulose is called hydrocellulose or oxycellulose, depending on the agent used for degradation. The term holocellulose is used to describe the residue after lignin has been removed from wood pulp.

Control of the regeneration conditions, together with a wide variety of modification, allows the production of a wide variety of products including high wet modulus fibers, hollow fibers, crimped fibers, and flame-resistant fibers. While almost all rayon is produced using the viscose process, some fibers are still produced using the cuprammonium process whereby cellulose is dissolved in an ammonium–copper II–alkaline solution.

4.3.2 WRINKLE-FREE FABRIC

Wrinkle-free or permanent press cotton is now an advertized property of many materials composed of cotton or regenerated cellulose. The idea of producing wrinkle-free fabrics is not new and



PICTURE 4.10 Cellophane wrapping.

TABLE 4.2 Noncellulosic Textile Fibers

Fiber Name	Definition	Properties	Typical Uses	Patent Names (Sample)
Acrylic	Acrylonitrile units, 85% or more	Warm, lightweight, shape retentive, resilient, quick drying, resistant to sunlight	Carpeting, sweaters, skirts, baby cloths, socks, slacks, blankets, draperies	Orlon
Modacrylic	Acrylonitrile units, 35%–85%	Resilient, softenable at low temperatures, easy to dye, abrasion resistant, quick drying, shape retentive, resistant to acids and bases	Simulated fur, scatter rugs, stuffed toys, paint rollers, carpets, hairpieces, wigs, fleece fabrics	Verel, Dynel
Polyester	Dihydric acid–terephthalic acid ester, 85% or more	Strong, resistant to stretching and shrinking, easy to dye, quick drying, resistant to most chemicals, easily washed, abrasion resistant; retains heat set (permanent press)	Permanent press ware, skirts, slacks, underwear, blouses, rope, fish nets, tire cord, sails, thread	Vycron, Kodel, Fortrel, Chemstrand Dacron
Spandex	Segmented polyurethane, 85% or more	Light, soft, smooth, resistant to body oils, can be stretched often, retain original form, abrasion resistant	Girdles, bras, slacks, bathing suits, pillows	Lycra
Nylon	Reoccurring amide groups	Very strong, elastic, lustrous, easy to wash, abrasion resistant, smooth, resilient, low moisture absorbency, recovers quickly from extensions	Carpeting, upholstery, blouses, tents, sails, hosiery, suits, tire cord, fabrics, rope, nets	Caprolan, Astroturf, Celanese polyester

TABLE 4.3 Cellulosic Fibers

Fiber Name	Definition	Properties	Typical Uses	Patent Names (Sample)
Rayon	Regenerated cellulose with less than 15% OH substituted	Highly absorbent, soft, comfortable, easy to dye, good drapability	Dresses, suits, slacks, blouses, coats, tire cord, ties, curtains, blankets	Avril, Cuprel, Zantel
Acetate	Not less than 92% OH groups acetylated	Fast drying, supple, wide range of dyeability, shrink resistant	Dresses, shirts, slacks, draperies, upholstery, cigarette filters	Estron, Celanese acetate
Triacetate	Derived from cellulose by combining with acetic acid and/or acetic anhydride	Resistant to shrinking, wrinkling, and fading; easily washed	Skirts, dresses, sportswear	Arnel

a scientific approach to achieve this began in the early 1900s. Scientists knew that cellulose chains were held together through hydrogen bonding. When a cotton fabric is permitted to remain in a dryer, worn, or kept in a drawer, the “ironed in” rearrangement of hydrogen bonds creating a somewhat smooth surface breaks and reforms generally creating wrinkles. Efforts began to create cross-links that attached the chains to one another after the surface was aligned giving desired creases and wrinkle-free surfaces. One of the earlier experiments employed urea-formaldehyde and similar cross-linkers. While these early treatments gave somewhat wrinkle-free fabrics, many caused color changes in the fabric when ironed or bleached giving a fabric with a yellow coloration because the chlorine in the bleach reacted with the amine groups in the cross-linkers.

By the 1960s, cotton fabrics accounted for about 80% of the wrinkle-free market. But synthetic fabrics such as polyesters and nylons started taking over the market. This encouraged cotton-related companies to develop additional cross-linkers. One such cross-linking agent was dimethylol dihydroxyethylene urea (DMDHEU) (4.7) developed by a group of researchers including Ruth Benerito and Noelle Bertoniere at the Department of Research Center Southern Regional Research Center in New Orleans. They recognized that cross-linking groups should take advantage of the hydrogen-bonding inherent in cellulose. DMDHEU had four hydroxyl groups capable of making use of hydrogen-bonding in cellulose. Today, DMDHEU is widely used as a finishing agent for cotton fabric.



There are problems. First, because treatment of colored fabric with DMDHEU occurs under acidic conditions, some weakening of the fabric occurs. Second, DMDHEU is synthesized using formaldehyde, which is one of the chemicals released as DMDHEU decomposes. While formaldehyde occurs naturally, it is a possible cancer-causing agent so its presence is undesirable. The amount of formaldehyde emitted by decomposing DMDHEU is limited through capping the cross-linking agent with alcohols.

Currently, research continues on developing “formaldehyde-free” cross-linking agents.

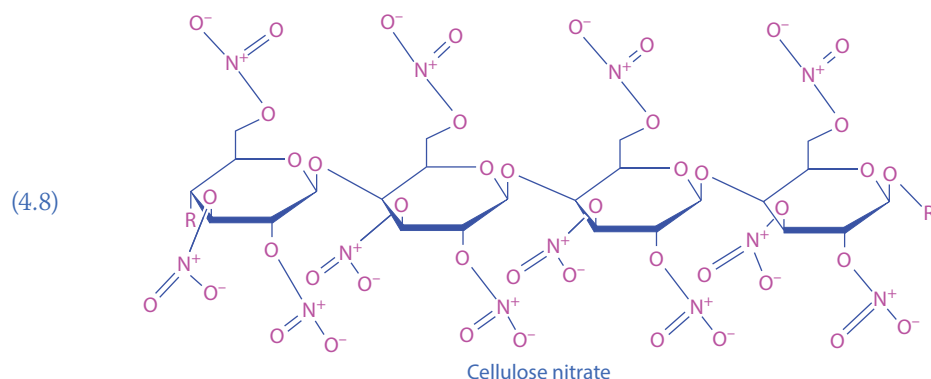
4.4 ESTERS AND ETHERS OF CELLULOSE

As noted before, the three hydroxyl groups on the individual cellulose rings are not equivalent. The two ring hydroxyls are acidic with pKa's similar to hydroquinone, while the third non-ring hydroxyl is similar to an aliphatic hydroxyl in acidity. Thus, in an aqueous sodium

hydroxide solution, the two ring hydroxyls will be deprotonated at high pHs. In theory, all three hydroxyls can undergo reaction, but in actuality, less than three undergo reaction either because of reactivity restrictions and/or because of steric limitations. With many of the electrophilic/nucleophilic reactions, it is the ring hydroxyls that are favored to react initially. The average number of hydroxyl groups that are reacted is often given as the *degree of substitution* or DS.

4.4.1 INORGANIC ESTERS

The most widely used so-called inorganic ester of cellulose is “cellulose nitrate” (CN), also called nitrocellulose and gun cotton. Celluloid is produced from a mixture of CN and camphor. CN was first made about 1833 when cellulose-containing linen, paper, or sawdust was reacted with concentrated nitric acid. It was the first “synthetic” cellulose recognized product. Initially, CN was used as a military explosive and improvements allowed the manufacture of smokeless powder. A representation of CN is given in Structure 4.8.



The development of solvents and plasticizing agents for CN led to the production of many new and useful nonexplosive products. Celluloid was produced in 1870 from a mixture of CN and camphor. Films were cast from solution and served as the basis for the original still and motion pictures. After World War I, the development of stable CN solutions allowed the production of fast-drying lacquer coatings.

While CN played an important role in the development of technology, its importance today is greatly diminished. It is still used as a protective and decorative lacquer coating, in gravure inks, in water-based emulsions as coatings, and to a lesser extent in plastics and films.

Cellulose phosphate esters are produced from reaction with phosphoric acid and urea. The products are used to treat hypercalciuria because of its ability to bind calcium. It has also been used for the treatment of kidney stones.

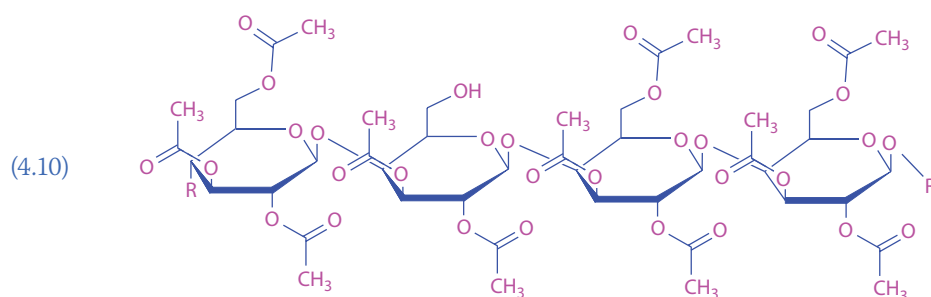
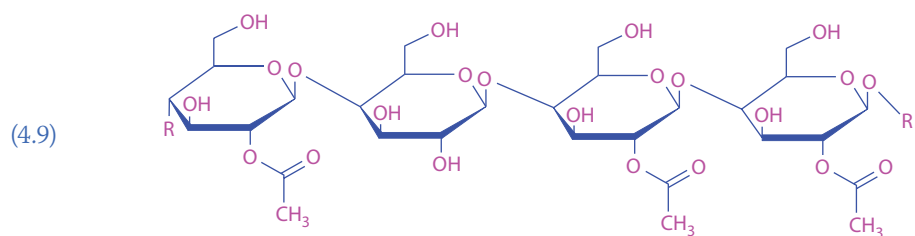
4.4.2 ORGANIC ESTERS

The most important cellulose ester is “cellulose acetate” because of its use in fibers and plastics. They were first made in 1865 by heating cotton with acetic anhydride. During World War I, a cellulose acetate replaced the highly flammable CN coating on airplane wings and fuselage fabrics.

Varying properties are achieved by varying the amount of substitution. The melting point generally decreases with decreasing acetylation. Lower acetylation gives products with greater solubility in polar solvents and corresponding decreased moisture resistance. Cellulose acetate is made using heterogeneous solutions containing the cellulose, sulfuric acid as the catalyst, and acetic anhydride in acetic acid. Reaction occurs beginning with the surface or outermost layer

and continues on layer by layer as new areas are exposed. When more homogeneous modification is desired, preswelling of the cellulose in water, aqueous acetic acid solutions, or in glacial acetic acid is carried out.

Reaction occurs differently since there are two “types” of hydroxyl groups (as noted before), the two ring hydroxyls and the methylene hydroxyl. In the typical formation of esters, such as cellulose acetate, the ring hydroxyl groups are acetylated initially (4.9) prior to the C-6 exocyclic hydroxyl. Under the appropriate reaction conditions, reaction continues to almost completion with all three of the hydroxyl groups esterified (4.10). In triacetate products, only small amounts (on the order of 1%) of the hydroxyls remain free and of these, generally about 80% are the C-6 hydroxyl.



Most common commercial products are the triacetate (DS approaching 3) and the secondary acetate (DS about 2.45).

While other organic esters are commercially available, namely, cellulose butyrate and cellulose propionate, by far the most widely used is cellulose acetate. Cellulose acetate is available as plastics, in films, as sheets, as fibers, and in lacquers. Cellulose acetate is used in the manufacture of display packaging and as extruded film for decorative signs and to coat a variety of fibers. Injected molded products include toothbrush handles, combs, and brushes. It is also used in lacquers and protective coatings for metal, glass, and paper. Cellulose acetate films are used in reverse osmosis to purify blood, fruit juices, and brackish water. Some eyeglass frames are made of cellulose acetate. Biodegradable film, sponges, and microencapsulation of drugs for control release also utilize cellulose acetate. Cellulose triacetate is used for photographic film bases. Numerous continuous filament yarns, tows, staples, and fibers are made from cellulose acetate. The precise form of filament produced is controlled by a number of factors including the shape of the die.

As in all large-scale industrial processes, the formation of the cellulose esters involves recovery of materials. Acetic anhydride is generally employed. After reaction, acetic acid and solvent are recovered. The recovered acetic acid is employed in the production of additional acetic anhydride. The recovered solvent is then reintroduced after treatment.

Cellulose esters are used as plastics for the formation by extrusion of films and sheets and by injection molding of parts. They are thermoplastics and can be fabricated employing most of the usual techniques of (largely compression and injection) molding, extrusion, and casting. Cellulose esters plastics are noted for their toughness, smoothness, clarity, and surface gloss.

Acetate fiber is the generic name of a fiber that is partially acetylated cellulose. They are also known as cellulose acetate and triacetate fibers. They are nontoxic and generally nonallergic so are ideal from this aspect as clothing material.

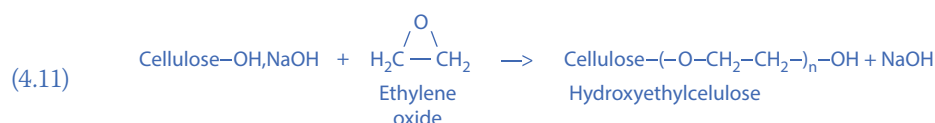
While acetate and triacetate differ only moderately in the degree of acetylation, this small difference accounts for differences in the physical and chemical behavior for these two fiber materials. Triacetate fiber is hydrophobic and application of heat can bring about a high degree of crystallinity that is employed to “lock in” desired shapes (such as permanent press). Cellulose acetate fibers have a low degree of crystallinity and orientation even after heat treatment. Both readily develop static charge and thus antistatic surfaces are typically employed to clothing made from them.

For clothing application, there are a number of important performance properties that depend on the form of the textile. These properties include wrinkle resistance, drape, strength, and flexibility. These properties are determined using American Society for Testing and Materials (ASTM) tests that often involve stress–strain behavior. Thus, the ability of a textile to resist deformation under an applied tensile stress is measured in terms of its modulus of elasticity or Young’s modulus. As with any area of materials, specialty tests are developed to measure certain properties. Some of these are more standard tests like the Young’s modulus mentioned earlier, while others are specific to the desired property measured for a specific application. For instance, resistance to slightly acidic and basic conditions is important for textiles that are to be laundered. Again, these are tested employing standard test procedures. In general, triacetate materials are more resistant than acetate textiles to basic conditions. Both are resistant to mild acid solutions but degrade when exposed to strong mineral acids. Further, behavior to various dry cleaning agents is important. As the nature of dry cleaning agents change, additional testing and modification in the fabric treatments are undertaken to offer a textile that stands up well to the currently employed cleaning procedures. Again, both are stable to perchloroethylene dry cleaning solvents but can soften when exposed to trichloroethylene for extended treatment. Their stability to light is dependent upon the wavelength, humidity present, etc. In general, they offer a comparable stability to light as that offered by cotton and rayon.

While cellulose acetates are the most important cellulose ester, they suffer by their relatively poor moisture sensitivity, limited compatibility with other synthetic resins, and relatively high processing temperature.

4.4.3 ORGANIC ETHERS

Reaction with an epoxide such as ethylene oxide under alkaline conditions gives “hydroxyethylcellulose” (HEC).



This is an S_N2 reaction with the reaction proportional to the concentration of the epoxide and alkali cellulose, but since the base is regenerated, it is first order in epoxide:

$$(4.12) \quad \text{Rate} = k [\text{Epoxide}]$$

Industrially, HECs with DS values below 2 are used. Low DS materials (to about 0.5) are soluble only in basic solutions while those with DS values of about 1.5 are water soluble. Concentrated solutions of HEC are pseudoplastic with their apparent viscosities decreasing with increased rates of shear. Dilute solutions approach being Newtonian in their flow properties, even under a wide range of shear rates.

HEC is used as a protective colloid in latex coatings and pharmaceutical emulsions; as a film former for fabric finishes and fibrous glass and in aerosol starches; as a thickener for adhesives, latex coatings, toothpaste, shampoos and hair dressings, cosmetic creams and lotions, inks, and joint cements; as a lubricant for wallpaper adhesives and in pharmaceutical gels; and as a water binding for cements, plastics, texture coatings, and ceramic glazes and in printing inks.

Sodium carboxymethylcellulose is formed by the reaction of sodium chloroacetate with basic cellulose solutions. The sodium form of carboxymethylcellulose is known as CMC or as a food-grade product as cellulose gum. It is soluble in both hot and cold water.

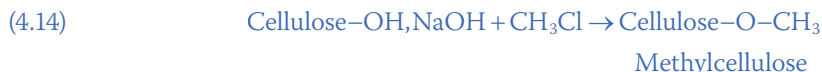


The most widely used cellulose gums have DS values about 0.65–1.0. CMCs are used as thickening, binding, stabilizing, and film-forming agents.

Carboxymethyl hydroxyethylcellulose is synthesized from the reaction of hydroxyethylcellulose with sodium chloroacetate. The product is a mixed ether. It has properties similar to both CMC and HEC. Like CMC, it exhibits a high water binding ability and good flocculating action on suspended solids but it is more compatible than CMC with salts. It forms ionic cross-links in the presence of salt solutions containing multivalent cations allowing its viscosity to be greatly increased by the presence of such cations. Solutions can be gelled by addition of solutions of aluminum and iron. It is a water-soluble material used in oil recovery and in hydraulic fracturing fluids.

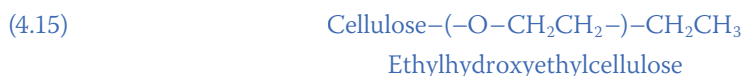
Methyl and hydroxyalkylmethylcelluloses are nonionic polymers soluble in cool water. Methylcellulose (MC), hydroxyethylmethylcellulose, and hydroxypropylmethylcellulose do not interact with cations forming insoluble salts, but electrolytes that compete with MC for water can cause precipitation.

MC is formed from basic cellulose and its reaction with chloromethane:



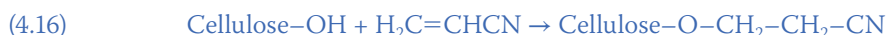
MC is used as an adhesive; in ceramics to provide water retention and lubricity; in cosmetics to control rheological properties and in the stabilization of foams; in foods as a binder, emulsifier, stabilizer, thickener, and suspending agent; in paints, paper products, and plywood as a rheology control for the adhesive; and in inks, in textiles as a binder, and for coatings.

Ethylhydroxyethylcellulose (EHEC) is a nonionic mixed ether available in a wide variety of substitutions with corresponding variations in aqueous and organic liquid solubilities. It is compatible with many oils, resins, and plasticizers along with other polymers such as nitrocellulose. EHEC is synthesized through a two-step process beginning with the formation of the HEC-like product through reaction between the basic cellulose and ethylene oxide. The second step involves further reaction with ethyl chloride:



Uses for the water-soluble EHEC include in waterborne paints, pastes, polymer dispersions, ceramics and cosmetics, and pharmaceuticals. Uses for organic soluble EHEC include in inks, lacquers, and as coatings.

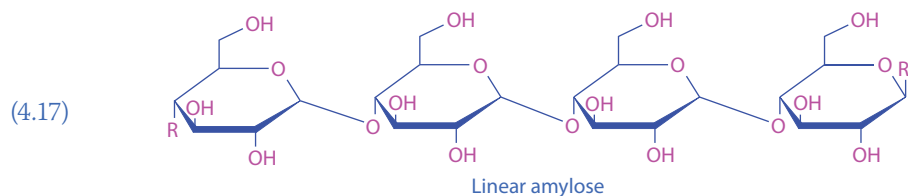
Cellulose undergoes reaction with activated ethylenic compounds such as acrylonitrile giving cyanoethylcellulose via a Michael addition.



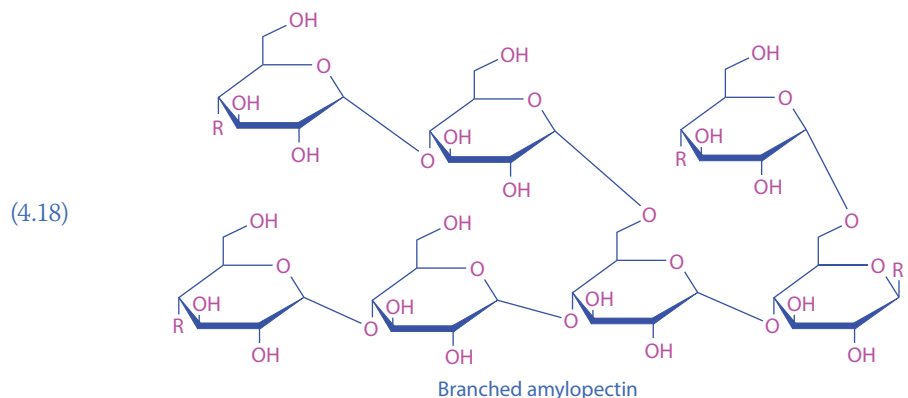
4.5 STARCH

While cellulose is the major structural polysaccharide, plant energy storage and regulation utilizes a combination of similar polysaccharides that combined are referred to as starch.

Starch can be divided into two general structures: branched *amylopectin* and largely linear *amylose*.



Most starches contain about 10%–20% amylose and 80%–90% amylopectin though the ratio can vary greatly. While cellulose can be considered a highly regular polymer of D-glucose with units linked through a β -1,4 linkage, amylose is a linear polysaccharide with glucose units linked in an α -1,4-fashion while amylopectin contains glucose units with chains of α -1,4 glucopyranosyl units but with branching occurring every 20–30 units, with the chain branch occurring from the 6 position. While this difference in orientation is how the glucose units are connected appears small, it causes great differences in the physical and biological properties of cellulose and starch. As noted before, people contain enzymes that degrade the α -glucose units but we are unable to digest β units. Thus, starch is a food source for us, but cellulose is not. Also, the individual units of cellulose can exist in the chair conformation with all of the substituents equatorial, yet amylose must either have the glycosyl substituent at the 1 position in an axial orientation or exist in a nonchair conformation.



Amylose typically consists of over 1000 D-glucopyranoside units. Amylopectin is a larger molecule containing about 6,000–1,000,000 hexose rings essentially connected with branching occurring at intervals of 20–30 glucose units. Branches also occur on these branches giving amylopectin a fan or treelike structure similar to that of glycogen. Thus, amylopectin is a highly structurally complex material. Unlike nucleic acids and proteins where specificity and being identical are trademarks, most complex polysaccharides can boast of having the “mold broken” once a particular chain was made so that the chances of finding two exact molecules are very low.

Commercially, starch is prepared from corn, white potatoes (Picture 4.11), wheat, rice, barely, millet, cassava, tapioca, and sorghum. The fraction of amylose and amylopectin varies between plant species and even within the same plant varies depending on location, weather, age, and soil conditions. Amylose serves as a protective colloid. Mixtures of amylose and amylopectin, found combined in nature, form suspensions when placed in cold water. Starch granules are insoluble in cold water but swell in hot water, first reversibly until gelatinization occurs at which point the swelling is irreversible. At this point, the starch loses its birefringence, the granules burst, and some starch material is leached into solution. As the water temperature continues to increase to near 100°C, a starch dispersion is obtained. Oxygen must be avoided during heating or oxidative degradation occurs. Both amylose and amylopectin are then water soluble at elevated temperatures. Amylose chains tend to assume a helical arrangement giving it a compact structure. Each turn contains six glucose units.

The ends of starch are the sites where degradation eventually to glucose begins. Because of the increased branching in amylopectin, it is able to more rapidly supply glucose in comparison



PICTURE 4.11 Potatoes are a good source of starch.

to amylase. You get an idea that glucose is being formed by placing some bread in your mouth for a few minutes, while the enzymes cause a breakdown to glucose indicated by a somewhat sweet taste.

The flexibility of amylose and its ability to take on different conformations are responsible for the “retrogradation” and gelation of dispersions of starch (Figure 4.3). Slow cooling allows the chains to align to take advantage of inter- and intrachain hydrogen bonding squeezing out the water molecules, leading to precipitation of the starch. This process gives retrograded starch, either in the presence of amylose alone or combined in native starch, which is more difficult

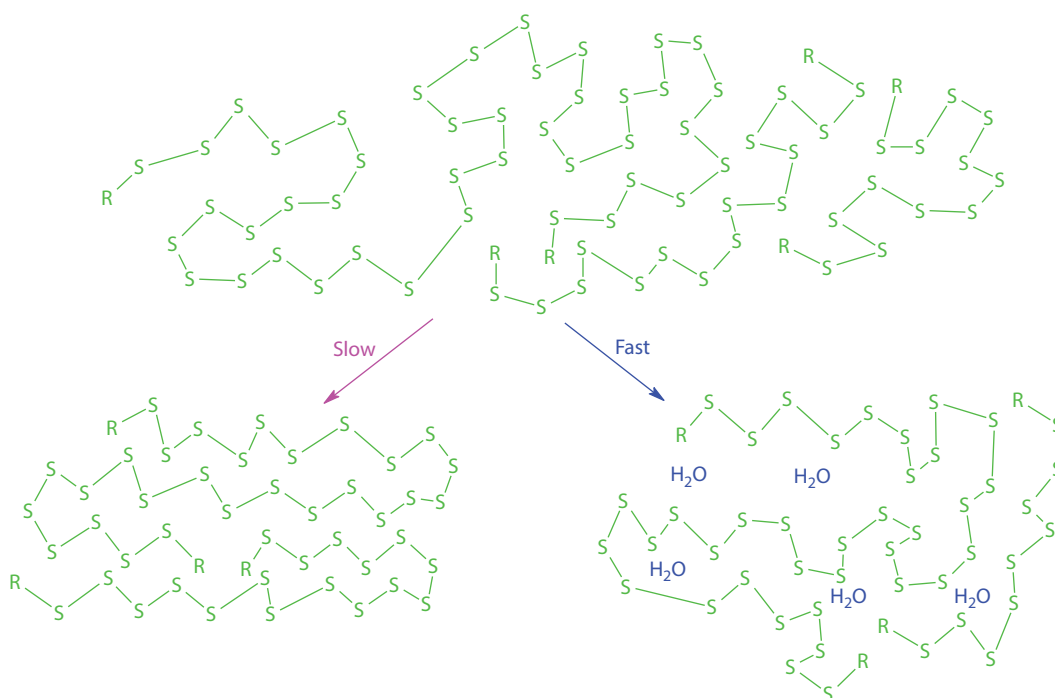


FIGURE 4.3 Behavior of amylose in a concentrated aqueous solution as a function of cooling rate.

to redisperse. Rapid cooling of starch allows some inter- and intrachain hydrogen bonding, but also allows water molecules to be captured within the precipitating starch allowing it to be more easily redispersed.

Most uses of starch make use of the high viscosity of its solutions and its gelling characteristics. Modification of starch through reaction with the hydroxyl groups lowers the gelation tendencies decreasing the tendency for retrogradation. Starch is the major source of corn syrup and corn sugar (dextrose or glucose). In addition to its use as a food, starch is used as an adhesive for paper and as a textile-sizing agent.

Oligomeric materials called “**cyclodextrins**” are formed when starch is treated with *Bacillus macerans*. These oligomeric derivatives generally consist of six, seven, eight, and greater numbers of glucose units joined through 1,4- α linkages to form rings. These rings are doughnut-like with the hydroxyl groups pointing upward and downward along the rim. Like crown ethers used in phase transfer reactions, cyclodextrins can act as “host” to “guest” molecules. In contrast to most phase transfer agents, cyclodextrins have a polar exterior and nonpolar interior. The polar exterior allows guest molecules to be water soluble. The nonpolar interior allows nonpolar molecules to also be guest molecules. Cyclodextrins are being used as enzyme models since they can first bind a substrate and through substituent groups and act on the guest molecule—similar to the sequence carried out by enzymes.

A major commercial effort is the free radical grafting of various styrenic, vinylic, and acrylic monomers onto cellulose, starch, dextran, and chitosan. The grafting has been achieved using a wide variety of approaches including ionizing and ultraviolet/visible radiation, charge-transfer agents, and various redox systems. Much of this effort is aimed at modifying the native properties such as tensile-related (abrasion resistance and strength) and care-related (crease resistance and increased soil and stain release) properties, increased flame resistance, and modified water absorption. One area of emphasis has been the modification of cotton and starch in the production of super-absorbent material through grafting. These materials are competing with all synthetic cross-linked acrylate materials that are finding use in diapers, feminine hygiene products, wound dressings, and sanitary undergarments.

4.6 OTHER POLYSACCHARIDES

The best-known homopolysaccharides are derived from D-glucose and known as glucans. Glucose has a number of reactive sites and a wide variety of polymers formed utilizing combinations of these reactive sites are found in nature. We have already visited the two most well-known members of this group—cellulose and starch containing amylose and amylopectin. Here we will visit some other important members.

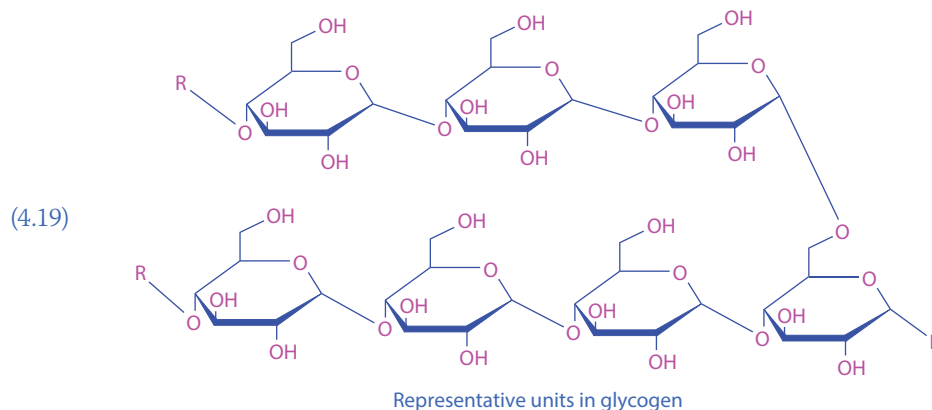
4.6.1 GLYCOGEN

Glycogen (4.19) is a very highly branched glucan or polysaccharide formed from glucose. It is structurally similar to amylopectin though more highly branched. This greater branching gives glycogen a greater water solubility. Glycogens are the principal carbohydrate food reserve materials in animals. They are found in both invertebrates and vertebrates and likely found in all animal cells. The highest concentration of glycogen is found in muscle with the greatest amount found in our liver, the tissue from which it is most often isolated.

Starch and glycogen are produced when the amount of glucose is high and are readily degraded back to glucose when energy is needed. In plants, this degradation occurs mainly through the action of two enzymes known as alpha- and beta-amylase. Interestingly, while the alpha-amylase can degrade starch and glycogen completely to glucose, beta-amylase is not able to degrade the branch points.

In animals, glycogen degradation to give the glucose needed as an energy source or to increase the blood sugar concentration begins with the action of phosphorylase. Phosphorylase occurs in active, a, and inactive, b, forms. Phosphorylase b is converted into phosphorylase a by phosphorylation that occurs at the end of a series of events initiated by an increased intercellular

concentration of cAMP and activation of the protein kinase (see Figure 4.8). This is reversed by a phosphoprotein phosphatase whose activity is hormonally regulated. Thus, phosphorylation initiated by increased intracellular concentrations of cAMP inactivates glycogen synthetase and activates phosphorylase. This is an example of the complex steps that are moment by moment carried out in our bodies. Here, enzymes that are responsible for the glycogen metabolism do not act directly on glycogen but regulate the activity of other enzymes.



Skeletal muscle glycogen delivers glucose primarily as a response to contractile stress. Regulation occurs through both modification of the enzyme phosphorylase, primarily by the action of epinephrine-adrenaline, and allosteric regulation of phosphorylase related to a demand for ATP. Glycogen found in the liver seldom is utilized as a source of energy but rather is employed to regulate blood sugar levels. Some tissues, such as nerve and brain tissue, rely solely on glucose as their energy source so that a steady supply of sugar is essential to their well-being.

4.6.2 DEXTRANS

Dextrans are high-molecular-weight-branched extracellular polysaccharides synthesized by bacteria. These bacteria are found in many places including the human mouth where they flourish on sucrose-containing food that becomes trapped between our teeth. The generated dextrans become part of the dental plaque and thus are involved in tooth decay. Dextran-causing bacteria can also infect sugarcane and sugar beets after harvest and act to not only decrease the yield of sucrose but also interfere with sugar refining clogging filters and pipelines. These bacteria can also contaminate fruit juices and wines, in fact any ready source of glucose or sucrose.

On the positive side, dextran itself has been refined and employed as a therapeutic agent in restoring blood volume for mass casualties. Natural dextrans are very high molecular weight (on the order of 10^8 – 10^9 Da) and are found to be unsuitable as a blood plasma substitute. Lower-molecular-weight (about 10^6 Da) dextran is suitable and is often referred to as clinical dextran.

Dextran gels are commercially used. The gel formed from reaction with epichlorohydrin gives a cross-linked material used as a molecular sieve. Commercial cross-linked dextran is known as Sephadex™ (Picture 4.12). Sephadex is formed in bead form from dissolving dextran in sodium hydroxide solution followed by dispersion in an immiscible organic liquid such as toluene containing poly(vinyl acetate) and finally added to epichlorohydrin. Different series of Sephadex are used industrially and in research. Ionic groups are often incorporated to give anionic and cationic dextrans and ion-exchange molecular sieves. Sulfate esters of dextran are also used in separations.

4.6.3 CHITIN

Chitin (4.20) is generally a homopolymer of 2-acetamido-2-deoxy-D-glucose (*N*-acetylglucosamine) 1 → 4 linked in a β configuration; it is thus an amino sugar analog of cellulose. While it is widely

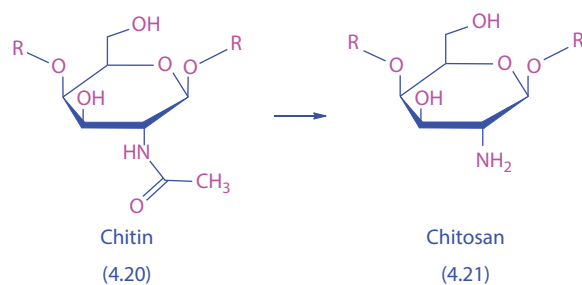


PICTURE 4.12 Sephadex column resin with some resin poured out.

distributed in bacteria and fungi, the major source is crustaceans. In fact, chitin is the most abundant organic skeletal component of invertebrates. It is believed to be the most widely distributed polysaccharide with the Copepoda alone synthesizing on the order of 10^9 tons each year. It is an important structural material often replacing cellulose in cell walls of lower plants. It is generally found covalently bonded to protein. Invertebrate exoskeletons often contain chitin that provides strength with some flexibility along with inorganic salts such as calcium carbonate that provide strength. In a real sense, this is a composite where the chitin holds together the calcium carbonate domains.

4.6.4 CHITOSAN

Chitosan (4.21) is produced from the deacetylation of chitin. Chitosan is employed in the food industry. It is a hemostatic from which blood anticoagulants and antithrombogenic agents have been formed. It is often sold as a body fat reducing agent or to be taken along with eating to encapsulate fat particles.



Both chitosan and chitin are greatly underused readily available abundant materials that deserve additional study as commercial materials and feedstocks. Chitin itself is not antigenic to human tissue and can be inserted under the skin or in contact with bodily fluids generally without harm. In the body, chitin is slowly hydrolyzed by lysozyme and absorbed. Chitin and chitosan can be safely ingested by us, and often we eat some since mushrooms, crabs, shrimp, many breads, and beer contain some chitin. Chitin and chitosan are believed to accelerate wound healing. Chitosan is also reported to exhibit bactericidal and fungicidal properties. Chitosan solutions are reported to be effective against topical fungal infections such as athlete's foot.

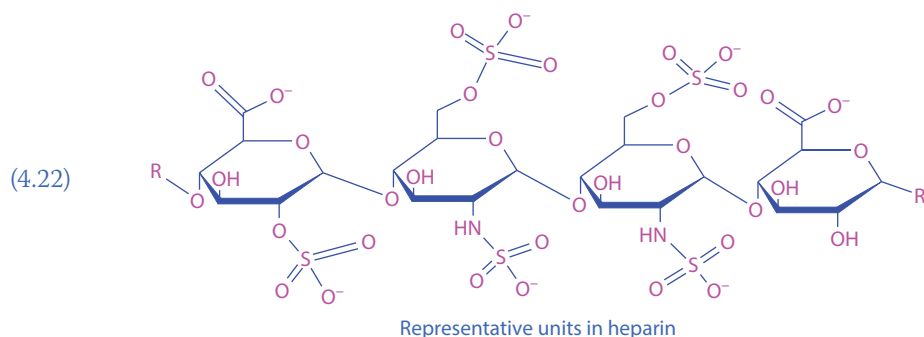
A continuing problem related to the introduction of bioengineering materials into our bodies is their incompatibility with blood. Many materials cause blood to clot (thrombosis) on the surfaces of the introduced material. Heparin is an anticoagulant, nontoxic material that prevents clot formation when coated on vascular implants. While chitosan is a hemostatic material (stops bleeding by enhancing clotting), chitosan sulfate has the same anticoagulant behavior as heparin.

Cardiovascular disease is the second leading cause of death in America. A contribution factor to cardiovascular disease is serum cholesterol. When ingested, chitosan exhibits hypocholesterolemic activity. Chitosan dissolves in the low pH found in the stomach and reprecipitates in the more alkaline intestinal fluid entrapping cholic acid as an ionic salt preventing its absorption by the liver. The cholic acid is then digested by bacteria in the large intestine. Chitosan may also act to increase the ratio of high-density lipoprotein to total cholesterol. Chitosan has been studied in the formation of films including membrane gels that immobilize enzymes and other materials because of the mild conditions under which they can be formed.

Chitosan has been used as a flocculate in wastewater treatment. The presence of the amine gives coacervation with negatively charged materials such as negatively charged proteins allowing removal of unwanted protein waste. The amine groups also capture metal ions, in particular polyvalent and heavy metal ions such as iron, lead, mercury, and uranium. Carraher, Francis, and Louda have also used chitosan to chelate with platinum salts to form materials with structures similar to the anticancer drug *cis*-dichlorodiammineplatinum II chloride. The amine and hydroxyl groups can be modified through the use of a wide range of reactions including formation of amides and esters.

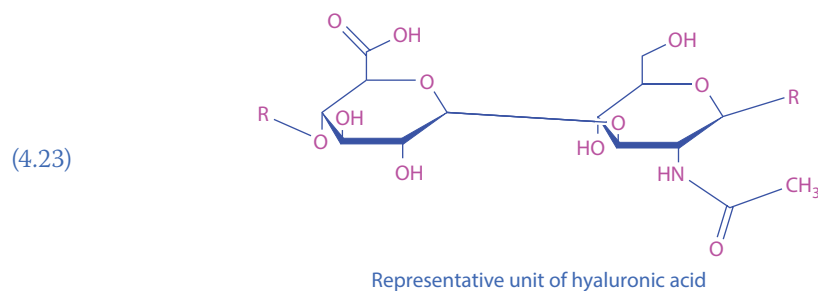
4.6.5 HEPARIN

Glycosaminoglycans are polysaccharides that contain amino sugar units. Most are of animal origin. *Heparin* (4.22) is complex containing D-glucuronic acid, L-iduronic acid, and D-glucosamine units. It is found in the lung, liver, and arterial walls of mammals. It is also found in intracellular granules of mast cells that line arterial walls and is released through injury. The glucuronic acid and iduronic acid units are not randomly present but occur in blocks. Heparin is found as the free polysaccharide and bonded to protein. Heparin acts as an anticoagulant, an inhibitor of blood clotting, and is widely used for this in medicine. In nature, its purpose appears to be to prevent uncontrolled clotting.



4.6.6 HYALURONIC ACID

Hyaluronic acid (4.23) is found in the connective tissues, umbilical cords, and skin, and it is the synovial fluid of joints. It can have very large molecular weights, to 10^7 Da making solutions of hyaluronic acid quite viscous. They can form gels. As a synovial fluid in joints, it acts as a lubricant and in the cartilage, it may also act, along with chondroitin sulfates, as a shock absorber. In some diseases, such as osteoarthritis, the hyaluronic acid of the joints is partially degraded resulting in a loss of elasticity of the area. The molecules can adopt a helical structure.



4.6.7 CHONDROITIN SULFATES

Chondroitin sulfates are found in the bone, skin, and cartilage but not as a free polysaccharide. Rather, it exists as proteoglycan complexes where the polysaccharide is covalently bonded to a protein. The proteoglycan of cartilage contains about 10% protein, keratan sulfate, and chondroitin sulfate, mainly the 4-sulfate in humans. The function of proteoglycan in cartilage is similar to that of noncellulosic polysaccharides and protein in plant cell walls. In cartilage, collagen fibers provide the necessary strength that is provided in plants by cellulose fibers. Thus, cartilage proteoglycan is an important part of the matrix that surrounds the collagen fibers giving it rigidity and incompressibility. This network can also act as a shock absorber since on compression the water is squeezed out to a nearby uncompressed region acting to “share the load” by distributing a shock or stress–strain. Chondroitin sulfate is sold as a health aid to “maintain healthy mobile joints and cartilage.”

4.6.8 ARABINOGALACTANS

Arabinogalactans contain unmodified galactose and is contained in many plant gums and carrageenan and agar. Seaweeds represent a source of many polysaccharides including alginic acid, agar, and carrageenan. Alginic acid is a polymer of D-mannuronic acid and L-guluronic acid that may be arranged in a somewhat random fashion or in blocks. It is used as a stabilizer for ice cream, in paper coating, in the manufacture of explosives, and in latex emulsions.

4.6.9 CARRAGEENANS, AGAR, AND AGAROSE

The *carrageenans* and *agar* are able to form double helices containing two parallel staggered chains creating a gel. There are three disaccharide units per helix turn. The sulfate units are located on the outside of the helix with the helical structure stabilized by internal hydrogen bonds. In nature, red seaweeds contain an enzyme that converts the galactose-6-sulfate of the k-carrageenan to 3,6-anhydrogalactose that causes a stiffening of the helix. It has been found that red seaweeds, found where there is strong wave action, contain a high proportion of hydrogalactose. Thus, it appears that the seaweed is able to control its structure in response to external stimuli to minimize shredding by the increased wave action. Because of its gelling ability, carrageenan is widely used as food thickeners and emulsion stabilizers in the food

industry and is present in many dairy products including less expensive ice cream and other dessert products providing a smooth, creamy texture. It is used as a stabilizer in foods such as chocolate milk.

Agar is employed as the basis of many microbiological media and in canned food because it can be sterilized. The latter is an advantage over gelatin that is not able to withstand sterilization. *Agarose* is the agar polysaccharide with the greatest gelling tendency. Agarose gels are employed in gel permeation chromatography and gel electrophoresis.

4.7 PROTEINS

4.7.1 BASICS

Many different monodisperse polymers of amino acids, which are essentially components of plants and animals, are called “**proteins**.” This word is derived from the Greek *porteios*, “of chief importance.” Twenty different α -amino acids are joined together by peptide linkages



and are also called polyamides or polypeptides. The latter term is often used by biochemists to denote oligomers or relatively low-molecular-weight proteins. (Note the structural similarities and differences between proteins and polyamides-nylons [Section 5.6].)

All α -amino acids found in proteins are of the general structure



except glycine

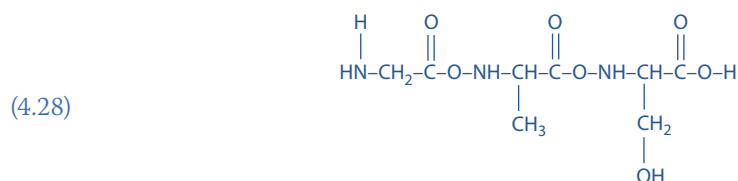


and contain a chiral carbon atom and are L-amino acids. They are all alpha-amino acids with the amine and acid moieties occurring on the same alpha carbon. The net ionic charge of an amino acid varies with the charges in the solution pH. The pH at which an amino acid is electrically neutral is called the “**isoelectric point**.” For simple amino acids (containing only one acid and one amine), this occurs at a pH of about 6 with the formation of a dipolar or **zwitterion** as shown here:



Hence, α -amino acids, like other salts, are water-soluble, high-melting, polar compounds that migrate toward an electrode at pH values other than that of the isoelectric point in a process called electrophoresis.

In writing out sequences for polypeptides, it is usual to use a three-letter abbreviation or a one-letter abbreviation starting with the N-terminus to the left and going to the C–O terminus to the right. Thus, the trimer

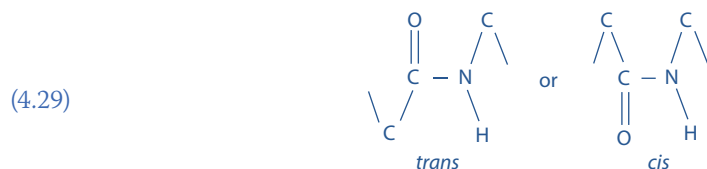


becomes Gly-Ala-Ser, GlyAlaSer, or EGAS where the E signals the N-terminus or GAS where the “G” is recognized as the N-terminus since by agreement the description is written from left (N-terminus) to right.

It is important to remember that all proteins are polypeptides. The size of proteins is generally noted in either the number of amino acid units or more likely the molecular weight in kilodaltons (kDa). Proteins are synthesized in nature from the N-terminus to the C-terminus.

The amino acids may be neutral, acidic, or basic, in accordance with the relative number of amino and carboxylic acid groups present. Cations can be formed with amino acids like tryptophane, lysine, histidine, and arginine that have “additional” amine groups, while others that contain “additional” acid groups can be hydrolyzed to form anions like aspartic acid and glutamic acid. The presence of varying amounts of these amino acid moieties within a protein is primary a driving force for the separation of proteins using electrophoresis and results in polypeptides having different isoelectric points. If there are a number of acidic and/or basic groups on the polypeptide, the molecule is said to be a *polyampholyte* or if they contain only positive or negative charges, they are called “*polyelectrolytes*.” The behavior of these charged polypeptides is similar to the behavior of other charged polymers. Thus, a fully hydrolyzed poly(acrylic acid) acts as a rod because the negative sites repel one another while a polypeptide with a large number of negative sites will also be elongated. The spacing and number of these charged sites helps determine the tertiary structure of such polypeptides.

Even though the atoms within a peptide bond are coplanar, they can exist in two possible configurations, *cis* and *trans*.



The *trans* form is usually favored whenever there is a bulky group on the adjacent alpha carbon(s) because the bulky groups offer less steric hindrance in the *trans* structure.

While humans synthesize about a dozen of the 20 amino acids needed for good health, the other 8 are obtained from outside our bodies, generally from eating foods that supply these *essential amino acids*. Different foods are good sources of different amino acids. Cereals are generally deficient in lysine. Thus, diets that emphasize cereals will also have other foods that can supply lysine. In the orient, the combination of soybean and rice supplies the essential amino acids while in Central Americas, bean and corn are used. There are a number of dietary sources of protein including those shown in Picture 4.13.

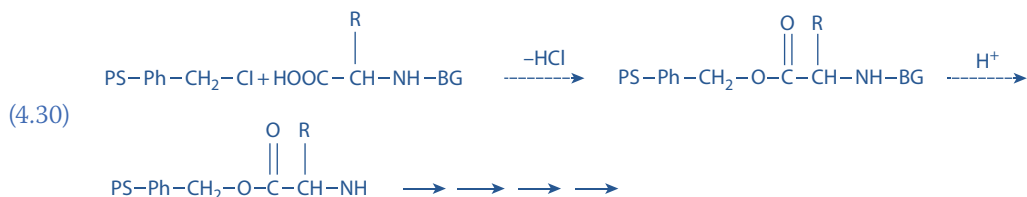
Almost all of the sulfur needed for healthy bodies is found in amino acids as cysteine and methionine. Sulfur serves several important roles including as a cross-linking agent similar to that served by sulfur in the cross-linking, vulcanization of rubber. This cross-linking allows the various chains that are connected by these cross-links to “remember” where they are relative to one another. This cross-linking allows natural macromolecules to retain critical shapes to perform necessary roles.

The most widely used technique for producing polypeptides with specific sequences is the solid-phase technique developed by Nobel Prize winner Bruce Merrifield in which all reactions take place on the surface of cross-linked polystyrene beads. The process begins with the attachment of the C-terminal amino acid to the chloromethylated polymer. Nucleophilic substitution by the carboxylate anion of an N-protected C-terminal amino acid displaces chloride from the chloromethyl group forming an ester, protecting the C site while attaching it to the



PICTURE 4.13 Sources of protein.

solid support. The blocking group is removed by addition of acid and the polymer containing the nonprotected N-terminus is washed to remove unwanted by-products. A peptide bond is formed by condensation to an N-blocked protected amino acid. Again, the solid-phase system is washed removing by-products. The blocking group is removed and the site is ready for attachment by another amino acid. This cycle is repeated eventually producing the desired polypeptide without isolation of intermediate products. These steps are outlined here:



where

PS is the polystyrene bead

Ph is the phenyl group

BG is the blocking group

The shapes of macromolecules, both synthetic and natural, can be described in terms of primary, secondary, tertiary, and quaternary structures (Figure 4.4). Protein structure will be used to illustrate these structures.

4.7.2 PRIMARY STRUCTURE

The term primary structure is used to describe the sequence of amino acid units (configuration) in a polypeptide chain. Thus, Equation 4.28 describes a primary structure.

4.7.3 SECONDARY STRUCTURE

The term “secondary structure” is used to describe the molecular shape or conformation of a molecule. The most important factor in determining the secondary structure of materials is its

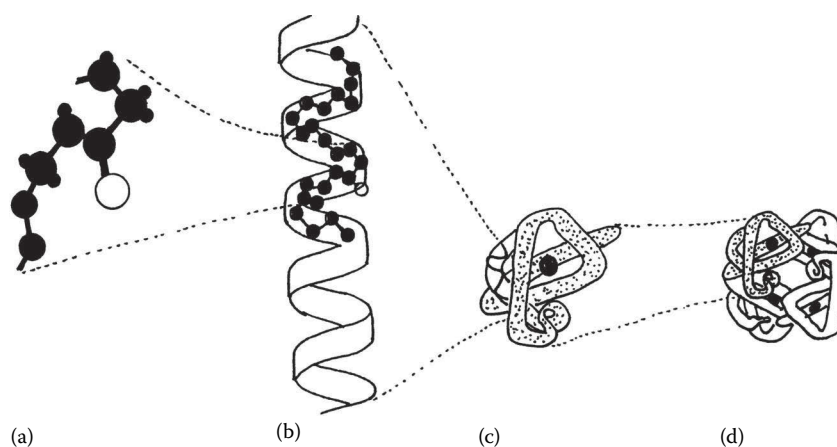


FIGURE 4.4 Four levels of structure elucidation. (a) Primary, (b) secondary, (c) tertiary, and (d) quaternary structures illustrate using a globular protein segment.

precise structure. For proteins, it is the amino acid sequence. Hydrogen bonding is also an important factor in determining the secondary structures of natural materials and synthetic materials that can hydrogen bond. In fact, for proteins, secondary structures are generally those that allow a maximum amount of hydrogen bonding. This hydrogen bonding also acts to stabilize the secondary structure, while cross-linking acts to lock in a structure.

In nature, the two most common secondary structures are helices and sheets. In nature, extended helical conformations appear to be utilized in two major ways: to provide linear systems for the storage, duplication, and transmission of information (DNA, RNA) and to provide inelastic fibers for the generation and transmission of forces (F-actin, myosin, and collagen). Examples of the various helical forms found in nature are single helix (messenger and ribosomal DNA), double helix (DNA), triple helix (collagen fibrils), and complex multiple helices (myosin). Generally, these helices are readily soluble in dilute aqueous solution. Often, solubility is only achieved after the inter- and intra-hydrogen bonding is broken.

There are a variety of examples in which linear or helical polypeptide chains are arranged in parallel rows. The two major forms that exist for proteins are illustrated in Figures 4.5 through 4.8. The chains can have the $N \rightarrow C$ directions running parallel making a parallel beta-sheet (Figure 4.6), or they can have the $N \rightarrow C$ directions running antiparallel giving antiparallel beta-sheets (Figure 4.7).

The structure of proteins generally falls into three groupings: fibers, membrane, and globular. The structural proteins such as the keratins, collagen, and elastin are largely fibrous. A reoccurring theme with respect to conformation is that the preferential secondary structures of fibrous synthetic and natural polymers approximate that of a pleated sheet (or skirt) or helix. The pleated sheet structures in proteins are referred to as beta arrangements (Figure 4.8). In general, proteins with bulky groups take on a helical secondary structure, while those with less bulky groups exist as beta-sheets.

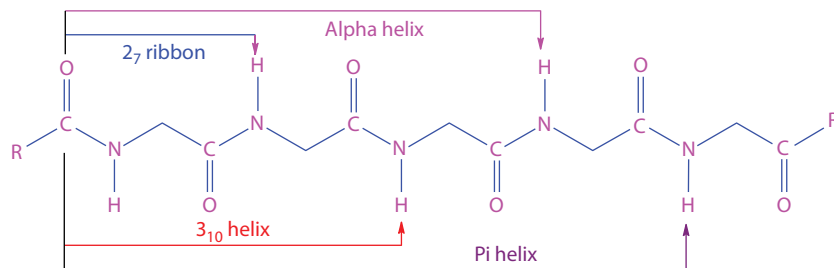


FIGURE 4.5 Commonly occurring repetitive helical patterns for polypeptides. (From Coates, J. and Carraher, C., *Polym. News*, 9(3), 77, 1983. With permission.)

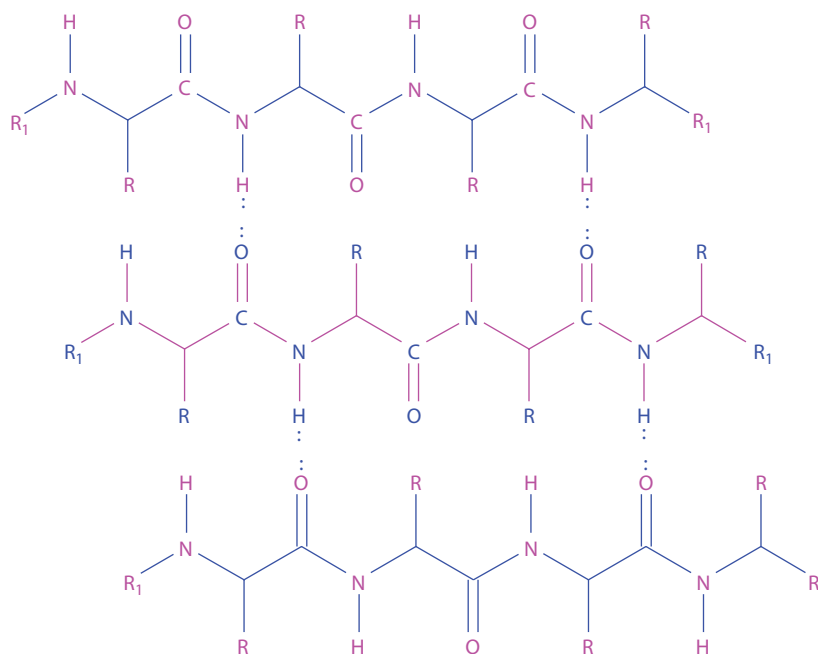


FIGURE 4.6 A beta arrangement or pleated sheet conformation of proteins.

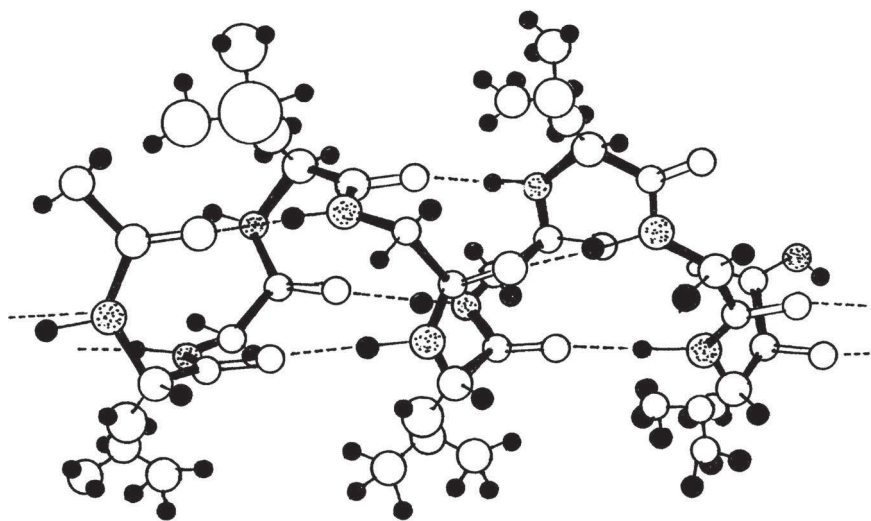


FIGURE 4.7 α -keratin helix for the copolymer derived from glycine and leucine.

Helices can be described by the number of amino acid residues in a complete “turn.” In order to fit into a “good” helix, the amino acids must have the same configuration. For proteins, that configuration is described as an L-configuration, with the helix being a “right-handed” helix. This right-handed helix is referred to as an **“alpha helix.”**

4.7.3.1 KERATINS

Keratins are structural proteins. As noted earlier, two basic “ordered” secondary structures predominate in synthetic and natural polymers. These are the helices and the pleated sheet structures. These two structures are illustrated by the group of proteins called the keratins. It is important to remember that hydrogen bonding is critical in both structures. For helices,

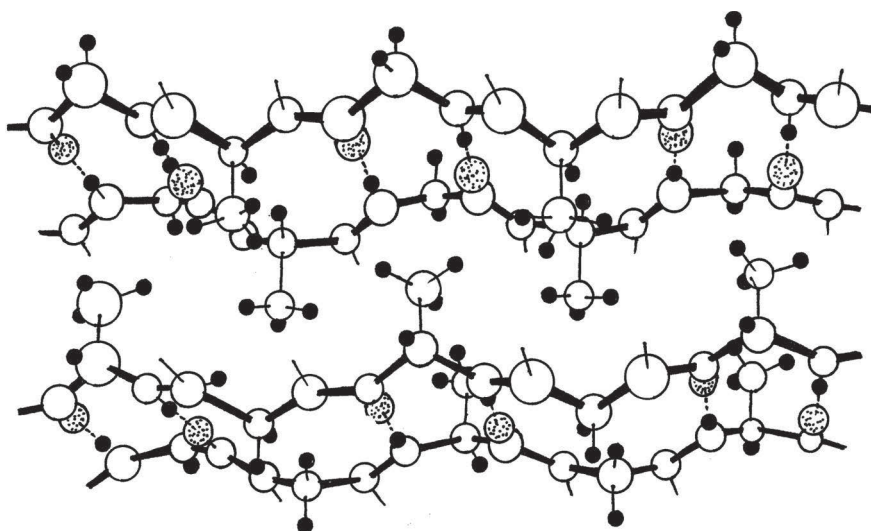


FIGURE 4.8 β -Keratin sheet for the copolymer derived from glycine and alanine.

the hydrogen bonding occurs within a single strand, whereas in the sheets, the hydrogen bonding occurs between adjacent chains.

Helices are often described in terms of a repeat distance, the distance parallel to the axis in which the structure repeats itself; pitch, the distance parallel to the helix axis in which the helix makes one turn; and rise, the distance parallel to the axis from the level of one repeat unit to the next (Figure 4.5).

Helices generally do not have an integral number of repeat units or residues per turn. The alpha helix repeats after 18 amino acid residues taking five turns to repeat. Thus, the number of residues per turn is $18/5 = 3.6$ residues/turn. For some polypeptides, each carbonyl oxygen is hydrogen bonded to the amino proton on the fourth residue giving a “hydrogen-bonded loop” with 13 atoms. Helices are often described in terms of this number, n . Thus, the alpha helix is described as a 3.6_{13} helix. Because hydrogen bonds tend to be linear, the hydrogen bonding in proteins approximate this with the $-N-H \cdots O=C$ in a straight line. The “rise,” h , of alpha-keratin (Figure 4.7) is found by x-ray spectroscopy to be about 0.15 nm for each amino acid residue. The pitch, p , of a helix is given by $p = nh$. For alpha-keratin, $p = 3.6$ amino acid residues/turn \times 0.15 nm/amino acid residue = 0.54 nm/turn.

Hair and wool are composed of alpha-keratin. A single hair on our head is composed of many strands of keratin. Coiled, alpha helices, chains of alpha-keratin intertwine to form protofibrils that in turn are clustered with other protofibrils forming a microfibril. Hundreds of these microfibrils, in turn, are embedded in a protein matrix giving a macrofibril that in turn combines giving a human hair. While combing will align the various hairs in a desired shape, after a while, the hair will return to its “natural” shape through the action of the sulfur cross-links pulling the hair back to its original shape.

Secondary bonding is involved in forming the helical structures allowing the various bundles of alpha-keratin to be connected by weak secondary interactions that in turn allow them to readily slide past one another. This sliding or slippage along with the “unscrewing” of the helices allows our hair to be flexible. Some coloring agents and most permanent waving of our hair involve breakage of the sulfur cross-links and a reforming of the sulfur cross-links at new sites to “lock in” the desired hair shape. Only a fraction of the sulfur cross-links are reformed by the “permanent” so that after some time, the original nonreformed cross-linked sites prevail and the hair returns to its original shape.

Our fingernails are also composed of alpha-keratin, but keratin with a greater amount of sulfur cross-links giving a more rigid material. In general, for both synthetic and natural polymers, increased cross-linking leads to increased rigidity.

4.7.3.2 SILK

The other major structural feature of proteins is pleated sheets. Two kinds of pleated sheets are found. When the chains have their $N \rightarrow C$ directions running parallel, they are called parallel beta-sheets. The $N \rightarrow C$ directions can run opposite to one another giving what is called an antiparallel beta-sheet. The beta-keratin (Figure 4.8) that occurs in silk produced by insects and spiders is of the antiparallel variety. While alpha-keratin is especially rich in glycine and leucine, beta-keratin is mostly composed of glycine and alanine with smaller amounts of other amino acids including serine and tyrosine. Size-wise, leucine offers a much larger grouping attached to the alpha carbon than does alanine. The larger size of the leucine causes the alpha-keratin to form a helical structure to minimize steric factors. By comparison, the smaller size of the alanine allows the beta-keratin to form sheets. This sheet structure is partially responsible for the “softness” felt when we touch silk. While silk is not easily elongated because the protein chains are almost fully extended, beta-keratin is flexible because of the low secondary bonding between sheets allowing the sheets to flow past one another.

In the silk fibroin structure, almost every other residue is glycine with either alanine or serine between them allowing the sheets to fit closely together. While most of the fibroin exists as beta-sheets, regions that contain more bulky amino acid residues interrupt the ordered beta-structure. Such disordered regions allow some elongation of the silk. Thus, in the crystalline segments of silk fibroin, there exists directional segregation using three types of bonding: covalent bonding in the first dimension, hydrogen bonding in the second dimension, and hydrophobic bonding in the third dimension. The polypeptide chains are virtually fully extended; there is a little puckering to allow for optimum hydrogen bonding. Thus, the structure is not extensible in the direction of the polypeptide chains. By comparison, the less specific hydrophobic (dispersive) forces between the sheets produce considerable flexibility. The crystalline regions in the polymers are interspersed with amorphous regions in which glycine and alanine are replaced by amino acids with bulkier pendant groups that prevent ordered arrangements from occurring. Furthermore, different silk-worm species spin silks with differing amino acid compositions and thus, with differing degrees of crystallinity. The correlation between the extent of crystallinity and the extension at the break point is given in Table 4.4.

For several thousand years, silk has been used in clothing, coverings, and other household items (Picture 4.14).

Another natural key that illustrates the tight relationship between structure and property is found in spider webs (Picture 4.15). The composition within a spider web is not all the same. We can look briefly at two of the general types of threads. One is known as the network or frame threads also called the dragline fabric. It is generally stiff and strong. The second variety is the catching or capture thread that is made of viscid silk that is strong, stretchy, and covered with droplets of glue. The frame threads are about as stiff as nylon 66 thread and on a weight basis stronger than steel cable. Capture thread is not stiff but is more elastomeric-like and on a weight basis about one-third as strong as frame thread. While there are synthetic materials that can match the silks in both stiffness and strength, there are few that come near the silk threads in toughness and their ability to withstand a sudden impact without breaking. Kevlar, which is used in bullet-resistant clothing, has less energy-absorbing capacity in comparison to either frame or capture threads. In fact, when weight is dropped onto frame silk, it adsorbs up to ten times more energy than Kevlar. On impact with frame thread, most of the kinetic energy dissipates as heat

TABLE 4.4 Selected Properties as a Function of Silk Worm Species

Silk Worm Species	Approximate Crystallinity (%)	% Extension at Break Point
<i>Anaphe moloneyi</i>	95	12.5
<i>Bombyx mori</i>	60	24
<i>Antheraea mylitta</i>	30	Flows then extends to 35%

Source: Coates, J. and Carraher, C., *Polym. News*, 9(3), 77, 1983. With permission.



PICTURE 4.14 Oil painting by the author on silk.



PICTURE 4.15 Semispiral orb spider web.

that, according to a hungry spider, is better than transforming it into elastic energy that might simply act to “bounce” the pray out of the web.

The frame threads are composed of two major components—highly organized microcrystals compose about one quarter of the mass and the other three quarters are composed of amorphous spaghetti-like tangles. The amorphous chains connect the stronger crystalline portions.

The amorphous tangles are dry and glass-like acting as a material below its T_g . The amorphous chains are largely oriented along the thread length as are the microcrystals giving the material good longitudinal strength. As the frame threads are stretched, the tangles straighten out allowing it to stretch without breaking. Because of the extent of the tangling, there is a lessening in the tendency to form micro-ordered domains as the material is stretched though that also occurs. Frame thread can be reversibly stretched to about 5%. Greater stretching causes permanent creep. Thread rupture does not occur until greater extension, such as 30%. By comparison, Kevlar fibers break when extended only 3%.

The capture threads are also composed of the same kinds of components but here, the microcrystals compose less than 5% of the thread with both the amorphous and microcrystalline portions arranged in a more random fashion within the thread. Hydrated glue, which coats the thread, acts as a plasticizer imparting to the chains a greater mobility and flexibility. The thread stretches several times its length when pulled and is able to withstand numerous shocks and pulls appropriate to contain the prey as it attempts to escape. Further, most threads are spun as two lines so the resulting thread has a kind of built-in redundancy.

The spinning of each type of thread comes from a different emission site on the spider, and the spider leaves little to waste, using unwanted and used web parts as another source of protein.

As with silk from silkworms, the fibers spun by spiders are also stronger than steel. In fact, the special accomplishments completed by Marvel Comic's Spiderman and his fiber shooter that allows him to swing from building to building and to stop trains are closer to reality than many of the comic-book superhero activities. By weight, spider silk is five times stronger than steel and three times tougher than Kevlar. Strength is defined as the area under a stress-strain plot and is roughly the weight that a material can hold without breaking. Toughness can be defined as the amount of kinetic energy a material can absorb without rupture. Chemically, this behavior is accomplished by a protein structure that is largely composed of repeated blocks of glycine and alanine. The smallness of the alpha-substituent on the central amino acid carbon allows a compact structure to be formed.

While native spider webs are desired, collecting such webs on a commercial scale is not practical if for no reason than spiders are loners and aggressive to one another. The spider web is so fine that it takes about 1500 strands to give one thread. Because of this, industry is developing new production techniques and spinning techniques similar to those required for microfibers.

Currently, efforts are underway to obtain spider web from alternative sources—namely, through use of genetic engineering, inserting the coding into *Escherichia coli* (*E. coli*) that expresses and produces that protein. Some approaches simply reproduce the *E. coli* using a fermentation process. Others are introducing the code into silkworms, alfalfa, and goats. For goats, the silk is captured as part of the goat's milk.

Companies are producing a variety of silk depending on the intended uses. Nonfibrous spider silk is being used in cosmetics such as shampoo where the silk binds to the hair's keratin allowing repair of the hair and making it more "silky." There are a number of "fiber" applications possible. Because the silk is not rejected by our bodies, it is being considered in the production of artificial tendons and to coat implants. Since its density is much less than copper but its heat conductivity is similar to copper, it is being considered where heat management is needed. Because of its high-impact strength, webs of fibers are considered in the manufacture of bullet-resistant materials. And because of its strength, production of cables is also being studied. Currently, cost and abundance are problems for wide-scale bulk application. But as in the case of microfibers, these are being overcome. Again, applications await our creativity.

The beta-keratin structure is also found in the feathers and scales of birds and reptiles.

We are beginning to understand better how we can utilize the secondary structure of polymers as tools of synthesis. One area where this is being applied is "folded oligomers." Here, the secondary structure of the oligomer can be controlled through its primary structure and use of solvents. Once the preferred structure is achieved, the oligomers are incorporated into larger chains eventually forming synthetic polymers with several precise structures "embedded" within them. The secondary structure of the larger polymers can also be influenced by the nature of the solvent allowing further structural variety. Further, other species, such as metal ions, can be added to assist in locking in certain desired structures and they can also be used to drive further structure modifications.

4.7.3.3 WOOL

Wool, while naturally existing in the helical form, forms a pleated skirt sheetlike structure when stretched. If subjected to tension in the direction of the helix axes, the hydrogen bonds parallel to the axes are broken and the structure can be irreversibly elongated to an extent of about 100%.

Wool is the fiber from members of the Caprinae family that includes sheep and goats (Picture 4.16). It is produced as an outer coat with the inner coat being more hairlike. Since it is removed without damaging the sheep's skin, it is renewable without sacrificing the animal. The fiber has two distinguishing characteristics that separate it from the fur and hair. It has scales that overlap like shingles on a roof and it is curly, with many fibers having over 20 bends per inch. This crimp has both advantages and disadvantages. The disadvantage is that the fiber tends to mat and gather cockleburrs when on the sheep. The curly nature gives the fiber lots of bulk and associated insulation ability. It retains air assisting the wearer to maintain their temperature. Thus, in the cold, the body retains needed heat, while in hot weather, the body can remain somewhat cool with respect to the surroundings. Thus, wool is a staple material for extreme temperatures.

The shingle nature results in a somewhat rough surface that helps the fibers to remain together. In turn, this allows the fibers to be easily formed into yarn.

As noted earlier, the inner coat is more hairlike with little scale or crimp. This hair is called kemp, while the fiber portion is the wool. Combined, they are referred to as the fleece.

A common theme with natural products is the variability of the fiber with the particular plant or animal and the particular conditions under which they were grown. The amount of kemp to wool varies from breed to breed as does the number of crimps per inch. Thus, wool from different breeds raised in different parts of the world will have different properties and contribution to different properties of the fiber. Generally, the wool and kemp are physically separated. In fact, after shearing, the wool is divided into five groups—fleece (which is the largest), pieces, bellies, crutchings, and locks. The last four are packaged and sold separately. The desired part, the fleece, is further classified.



PICTURE 4.16 Sheep produce wool in multiple thicknesses, lengths, and tensile strengths based on breed, environment, and diet. Above pictured is Cheviot sheep. The Cheviot wool is medium coarse wool about 31–32 μm in thickness, with a helix configuration that yields superb resilience that is high in tensile strength and has exceptional staple length. Cheviot wool is used primarily for Tweed but is also highly sought after as a blending wool to fortify other softer fibers.



PICTURE 4.17 Portion of a wool rug.

As the wool is removed from the sheep, it contains a high amount of grease that contains valuable lanoline. Natives make yarns out of this wool. But for most commercial use, the lanolin is removed by washing with detergents and basic solutions.

A number of different wools are special and sold under different names such as cashmere wool. These wools have their own special characteristics that increase their cost and value. It is interesting that many animals have developed their own special coats to overcome their native environment. Thus, because cashmere goats live in a cold mountain temperature, their wool is an effective material to protect against the cold.

Wool is used for a variety of purposes including clothing and carpets (Picture 4.17).

As an aside, wool is self-extinguishing so that flame retardants are not needed in wool rugs and suits. Further, we need not worry about herds of flammable sheep running about the hillsides.

4.7.4 TERTIARY STRUCTURE

The term “tertiary structure” is used to describe the shaping or folding of macromolecules. These larger structures generally contain elements of the secondary structures. Often, hydrogen bonding, salt bridges, post-translational modifications, and disulfide cross-linking lock in such structures (Figure 4.9). As noted earlier, proteins can be divided into three broad groups—fibrous or fibrillar proteins, membrane proteins, and globular proteins.

4.7.4.1 GLOBULAR PROTEINS

There is a wide variety of the so-called globular proteins. Almost all globular proteins are soluble in acidic, basic, or neutral aqueous solutions. Many globular proteins are enzymes. Many of these have varieties of alpha- and beta-structures imbedded within the overall globular structure. Beta-sheets are often twisted or wrapped into a “barrel-like” structure. They contain portions that are beta-sheet structures and portions that are in an alpha-conformation. Further, some portions of the globular protein may not be conveniently classified as either an alpha- or beta-structure.

These proteins are often globular in shape so as to offer a different “look” or polar nature to its outside. Hydrophobic residues are generally found in the interior, while hydrophilic residues are found on the surface interacting with the hydrophilic water-intensive external environment.

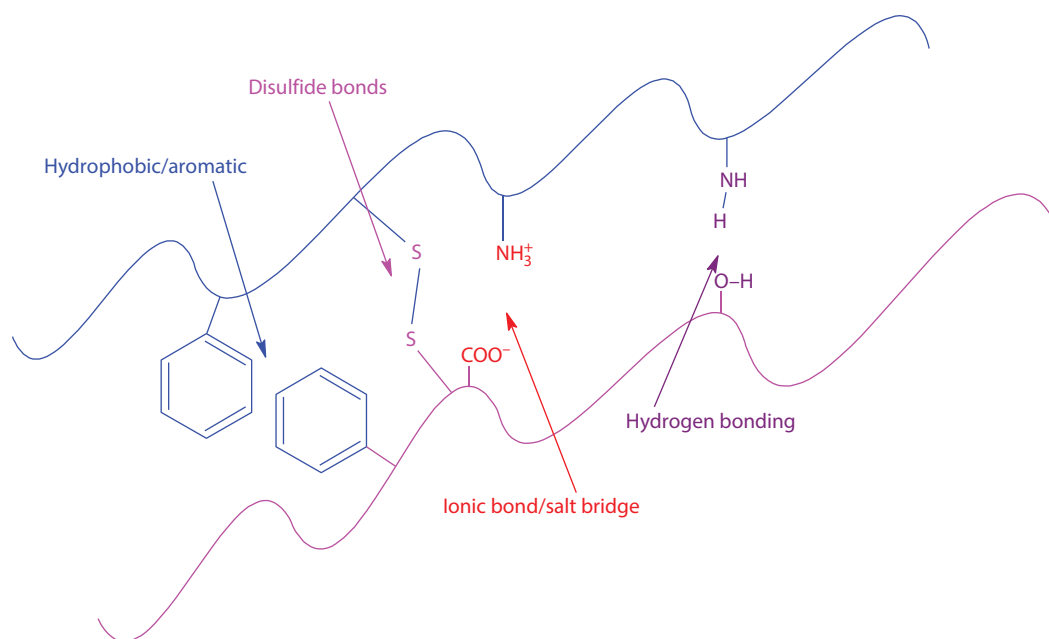


FIGURE 4.9 Chemical forces that help maintain the tertiary structure of proteins.

(This theme is often found for synthetic polymers that contain both polar and nonpolar portions. Thus, when polymers are formed or reformed in a regular water-filled atmosphere, many polymers will favor the presence of polar moieties on their surface.)

Folding depends on a number of interrelated factors. The chain-folding process involves going from a system of random beta and alpha-conformations to a single folded structure. This change involves a decrease in the entropy or randomness. In order for folding to occur, this increase in order must be overcome by energy-related factors to allow the overall free energy to be favorable. These energy factors include charge–charge interactions, hydrogen bonding, van der Waals interactions, and hydrophilic/hydrophobic effects.

Within a particular globular polymer, there may be one or more polypeptide chain folded backward and forward forming quite distinct structural domains. Each domain is characterized by a particular style of coiling or “sheeting” that may be nonrepetitive with respect to its peptide chain geometry or may be repetitive, conforming to one of several now well-recognized patterns. The specific chain conformations are determined by the side-chain interactions of the amino acids superimposed on intra-peptide hydrogen bonding along the chain. The form of chain folding is thus ultimately determined by the amino acid sequence and the polymeric nature of the polypeptide chains and is fundamental to the specific geometry of the given protein.

Protein units can be either negatively or positively charged. Attractions between unlike charges are important as are the repulsions between like charged units. As expected, these associations are pH dependent and are one route for conformation changes to occur. The ability to hydrogen bond is also an important factor with respect to the internal folding scheme. Because the proteins are tightly packed, the weak van der Waals interactions can also play an important role in determining chain folding. The tendency for polarity-like segments to congregate can also be an important factor in chain folding. Thus, hydrophilic groupings generally are clustered to the outside of the globular protein allowing them to take advantage of hydrogen bonding and other polar-bonding opportunities, while hydrophobic clusters of amino acid units occupy the internal regions of the protein taking advantage of hydrophobic interactions.

Globular proteins act in maintenance and regulatory roles—functions that often require mobility and thus some solubility. Included within the globular grouping are enzymes, most hormones, hemoglobin, and fibrinogen that are changed into an insoluble fibrous protein fibrin that causes blood clotting.

Denaturation is the irreversible precipitation of proteins caused by heating, such as the coagulation of egg white as an egg is cooked, or by addition of strong acids, bases, or other chemicals.

This denaturation causes permanent changes in the overall structure of the protein, and because of the ease with which proteins are denatured, it makes it difficult to study “natural” protein structure. Nucleic acids also undergo denaturation.

Small changes in the primary structure of proteins can result in large changes in the secondary structure. For instance, researchers have interchanged the positions of two adjacent amino acid residues of a globular protein portion resulting in a beta-strand becoming a right-handed helix.

Molecular recognition is one of the keys to life. Scientists are discovering ways to both modify molecular recognition sites and to “copy” such sites. One approach to modifying molecular recognition sites, namely, enzymatic protein sites, is through what is referred to as “[directed evolution](#).” Arnold and coworkers have employed the combinatorial approach by taking an enzyme with a desired catalytic activity and encouraging it to undergo mutation, selecting out those mutations that perform in the desired manner, and repeating this cycle until the new enzymes perform as desired. Ratner and coworkers have taken another approach whereby templates containing the desired catalytic sites are made. First, the protein is mounted on a mica support. The target protein is coated with a sugar monolayer that allows for specific recognition. A fluoropolymer plasma film is deposited over the sugar monolayer. The fluoropolymer reverse image is attached to a support surface using an epoxy resin. Solvents are then added to etch away the mica, sugar, and original protein leaving behind a “nanopit” template that conforms to the shape of the original protein.

[Enzymes](#) generally act to lower the activation energy through a combination of actions including holding the reactants in the correct geometry making the number of “hits” or connections necessary to achieve the products much less. The increases in reaction rate are generally huge. In the case of the enzyme orotate decarboxylase, the increase is 10^{17} allowing a reaction that might take 80 million years without the enzyme to occur in about 20 ms in the presence of the enzyme. There are about 4000 reactions known to be catalyzed by enzymes within the human body. While the size of the enzyme is large, the active site is generally only 3–4 amino acid units long. Enzymes are involved with much of our metabolism and are involved in the synthesis and repair of DNA and in transcription.

4.7.4.2 FIBROUS PROTEINS

Fibrous proteins are long macromolecules that are attached through either inter- or intrahydrogen bonding of the individual residues within the chain. Solubility, partial or total, occurs when these hydrogen bonds are broken. In general, they confer stiffness and rigidity to biological systems that are themselves fluid.

Fibrous proteins are found in animals. They appear as filaments and are often formed from a limited number of amino acid units. They are generally insoluble in water with hydrophobic portions protruding from the central core. Examples are collagen, elastin, and keratin. Actin and tubulin are globular soluble monomers that polymerize forming long stiff structures that make up the cytoskeleton that allows cells to maintain their shape. Structural proteins are used to construct tendons, bone matrices, connective tissues, and muscle fiber. They can also be used for storage. They are not as easily denatured as globular proteins.

Some structural proteins, such as kinesin, dynein, and myosin, serve as the so-called motor proteins that can generate mechanical forces as muscles and are involved in allowing the movement of cells such as the sperm cell involved in sexual reproduction in multicellular organisms.

[Collagen](#) is the most abundant single protein in vertebrates making up to one-third of the total protein mass. Collagen fibers form the matrix or cement material in our bones where mineral materials precipitate. Collagen fibers constitute a major part of our tendons and act as a major part of our skin. Hence, it is collagen that is largely responsible for holding us together. Collagen is also widely used in foods under the name gelatin (Picture 4.18).

The basic building block of collagen is a triple helix of three polypeptide chains called the “[tropocollagen unit](#).” Each chain is about 1000 residues long. The individual collagen chains form left-handed helices with about 3.3 residues per turn. In order to form this triple-stranded helix, every third residue must be glycine because it offers a minimum of bulk. Another interesting theme in collagen is the additional hydrogen bonding that occurs because of the presence of



PICTURE 4.18 Gelatin derived from collagen as thickening agent in popular gelatins. (From Shutterstock, <http://www.shutterstock.com/pic.mhtml?id=157568021&src=id>.)

hydroxyproline derived from the conversion of proline to hydroxyproline. The conversion of proline to hydroxyproline involves vitamin C. Interestingly, scurvy, the consequence of a lack of vitamin C, is a weakening of collagen fibers giving way to lesions in the skin and gums and weakens blood vessels. Collagen fibers are strong. In tendons, the collagen fibers have strength similar to that of hard-drawn copper wire.

Much of the toughness of collagen is the result of the cross-linking of the tropocollagen units to one another through a reaction involving lysine side chains. Lysine side chains are oxidized to aldehydes that react either with a lysine residue or with one another lysine through an aldol condensation and dehydration resulting in a cross-link. This process continues throughout our life resulting in our bones and tendons becoming less elastic and more brittle. Again, a little cross-linking is essential, but more cross-linking leads to increased fracture and brittleness.

Collagen is a major ingredient in some “gelation” materials. Here, collagen forms a triple helix for some of its structure, while other parts are more randomly flowing single collagen chain segments. The bundled triple helical structure acts as the rigid part of the polymer, while the less ordered amorphous chains act as a soft part of the chain. The triple helix also acts as a noncovalently bonded cross-link.

4.7.4.3 ELASTIN

Collagen is found where strength is needed, but some tissues, such as arterial blood vessels and ligaments, need materials that are elastic. Elastin is the protein of choice for such applications. Elastin is rich in glycine, alanine, and valine and it is easily extended and flexible. Its conformation approaches that of a random coil so that secondary forces are relatively weak allowing elastin to be readily extended as tension is applied. The structure also contains some lysine side chains that are involved in cross-linking. The cross-linking is accomplished when four lysine side chains are combined to form a desmosine cross-link. This cross-link prevents the elastin chains from being fully extended and causes the extended fiber to return to its original dimensions when tension is removed. One of the areas of current research is the synthesis of polymers with desired properties based on natural analogs. Thus, elastin-like materials have been synthesized using glycine, alanine, and valine and some cross-linking. These materials approach elastin in its elasticity.

4.7.4.4 MEMBRANE PROTEINS

Membrane proteins are attached to or associated with the membrane of a cell. More than half of the proteins interact with these membranes. Membrane proteins are generally divided according to their attachment to a membrane. Transmembrane proteins span the entire membrane. Integral proteins are permanently attached to only one side of membranes. Peripheral membrane proteins are temporarily attached to integral proteins or lipid bilayers through combinations of noncovalent bonding such as hydrophobic and electrostatic bonding. These membranes often act as receptors or provide channels for charged or polar molecules to pass through them.

4.7.5 QUATERNARY STRUCTURE

The term quaternary structure is employed to describe the overall shape of groups of chains of proteins or other molecular arrangements. For instance, hemoglobin is composed of four distinct but different myoglobin units, each with its own tertiary structure that comes together giving the hemoglobin structure.

Both synthetic and natural polymers have superstructures that influence/dictate the properties of the material. Many of these primary, secondary, tertiary, and quaternary structures are influenced in a similar manner. Thus, primary structure is a driving force for secondary structure. Allowed and preferred primary and secondary bonding influence structure. For most natural and synthetic polymers, hydrophobic and hydrophilic domains tend to cluster. Thus, most helical structures will have either a somewhat hydrophobic/hydrophilic inner core or the opposite outer core resulting from a balance between secondary and primary bonding factors and steric and bond angle constraints. Nature has used these differences in domain character to help create the world about us.

As noted before, some proteins are linear with inner and intrachain associations largely occurring because of hydrogen bonding. Influences on globular protein structures are more complex, but again, the same forces and features are at work. Globular proteins have irregular 3D structures that are compact but which when brought together form quaternary structures that approach being spherical. While the overall structure is spherical, the surface is irregular, with the irregularity allowing the proteins to perform specific biological functions.

The preferred folding confirmation is again influenced by the same factors of bonding type, polarity, size, flexibility, and preferred bond angles. The folded conformations are possible because of the flexibility of the primary bonding present within proteins. Thus, polar portions, namely, the amine and carbonyl moieties, are more fixed, but the carbon between them is more flexible. Again, the folding characteristic conformations are driven by secondary bonding. Some folding is chemically “fixed” through use of cross-links. In hair, these cross-links are often disulfides, $-S-S-$.

As noted before, the flexibility of proteins allows them to carry out a wide variety of tasks and the building sites of proteins produce a variety of different proteins. Our cells often build about 60,000 different kinds of proteins. By comparison, a bacterial cell will synthesize only a little over 1000 different kinds of proteins.

When a protein contains roughly more than about 200 amino acid groups, it often assumes two or more somewhat spherical tertiary structural units. These units are often referred to as domains. Thus, hemoglobin is a combination of four myoglobin units with each of the four units influenced by the other three and where each unit contains a site to interact with oxygen.

The specificity of enzymatic catalytic activity is dependent on tertiary structure. Phosphoglycerate kinase (Figure 4.10) is a protein composed of 415 amino acids. The protein chain is folded back and forward forming a claw-like structure that has two rigid domains divided by a more flexible hinge region. Phosphoglycerate kinase binds to phosphoglycerate, a fragment of glucose, transferring the phosphate forming ATP. If the enzyme binds to the phosphoglycerate and water, the phosphate could react with the water rather than forming ATP. The protein is designed to circumvent this by having the essential parts present in both halves of the claw.

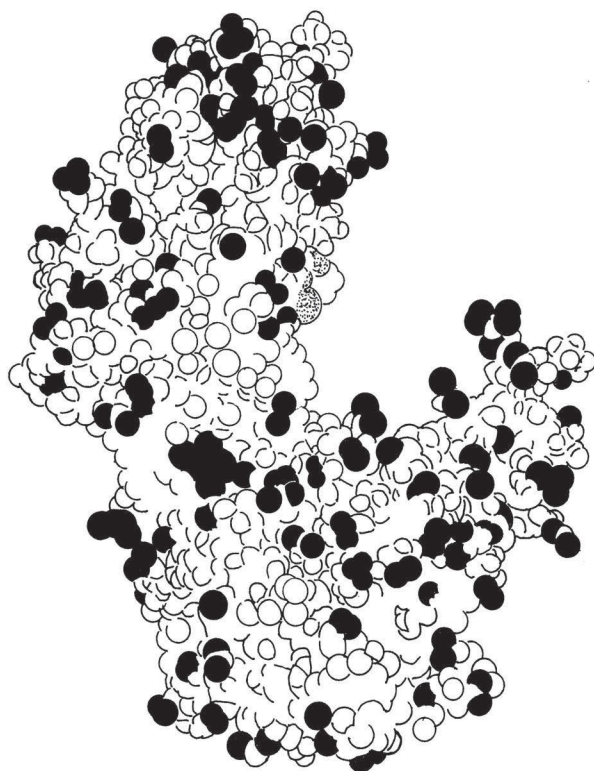


FIGURE 4.10 Protein enzyme phosphoglycerate kinase involved in the formation of adenosine-5'-triphosphate from adenosine-5'-diphosphate.

As the enzyme binds the phosphoglycerate and the ADP, the claw closes bringing together the two necessary active parts, excluding water and other nonessential compounds. In Figure 4.10, the active site phosphoglycerate is indicated by the “dotted” area about halfway up one of the two sections of the claw.

Figure 4.10 also illustrates the usual arrangement whereby hydrophilic areas, noted as darkened areas, radiate outward from the enzyme surface while the less hydrophilic and hydrophobic areas tend to reside within the enzyme.

Table 4.5 contains a list of some important proteins. Protein purification must be done under conditions where conformational and configurational changes are minimal. Such purification is most often carried out using varieties of chromatography including affinity chromatography and electrophoresis. Somewhat common features of enzymes are the following:

1. α -Helix content is not as high as in myoglobin, but areas of β -sheeting are not unusual.
2. Water-soluble enzymes have a large number of charged groups on the surface and those not on the surface are involved in the active site. Large parts of the interior are hydrophobic.
3. The active site is found either as a cleft in the macromolecule or shallow depression on its surface.

While enzymes are effective catalysts inside in the body, we have developed techniques for “capturing” some of this activity by immobilizing enzymes. The activity of many enzymes continues in this immobilized condition. In one approach, the enzyme is isolated and coupled to solvent-swelling gels using polyacrylamide copolymers that contain *N*-acryloxysuccinimide repeat units. The pendant groups react with the amino “ends” of the enzyme effectively coupling or immobilizing the enzyme. Modifications of this procedure have been used to immobilize a wide variety of enzymes. For instance, the particular reactive or anchoring group on the gel can be

TABLE 4.5 Shapes of Selected Biologically Important Proteins

Protein	Shape	Molecular Wt.	Comments
Myoglobin	3D, oblate spheroid	1.7×10^4	Temporary oxygen storage in muscles
Hemoglobin	3D, more spherical than myoglobin	6.4×10^4	Oxygen transport through body
Cytochrome C	3D, prolate spheroid	$1.2\text{--}1.3 \times 10^4$	Heme-cont. protein, transports electrons rather than oxygen
Lysozyme	3D, short α -helical portions, region of antiparallel pleated sheets	1.46×10^4	Well studied, good illustration of structure activity
Chymotrypsin and trypsin	3D, extensive β -structure	—	Hydrolysis of peptide bonds on the carboxyl side of certain amino acids
Insulin	3D, two α -helical section in A chain, B chain has α -helix and remainder is extended linear central core	6×10^3	Regulation of fat, carbohydrate, and amino acid metabolism
Somatotropin (human)	3D, 50% α -helix	2.2×10^4	Pituitary hormone
Collagen			
Keratin	Varies with source, 3D or 2D; most contain α -helix sections	$10^4\text{--}10^5$	Most abundant protein; major part of skin, teeth, bones, cartilage, and tendon
Fibroin	Varies with source, fibrous linear with cross-links; crystalline regions contain antiparallel, pleated sheets	3.65×10^5	Major constituent of silk
Elastin	Varies with source; cross-linked, mostly random coil with some α -helix	$>7 \times 10^4$	Many properties similar to rubber; gives elasticity to arterial walls and ligaments

especially modified for a particular enzyme. Spacers and variations in the active coupling end are often employed. Amine groups on gels are easily modified to give other functional groups including alcohols, acids, nitriles, and acids. Recently, other entities, such as fungi, bacteria, and cells, have been immobilized successfully. This technique allows the continuous synthesis of specific molecules.

4.8 NUCLEIC ACIDS

4.8.1 BASICS

The name “nuclein” was coined by Miescher in 1869 to describe products isolated from the nuclei in pus. This name was later changed to nucleic acid. Somewhat pure nucleic acid was isolated by Levene in the early 1900s. He showed that either D-ribose or D-deoxyribose (Figure 4.11) was present in what are now known as ribonucleic acid (RNA; containing the ribose sugar) and deoxyribonucleic acid (DNA; containing the deoxyribose sugar that contains a hydrogen on carbon 2 rather than a hydroxyl that is present in the ribose sugar). These specific compounds were originally obtained from yeast (DNA) and the thymus gland (RNA). Nucleic acids consist of these two sugars each containing an organic base called a purine or pyrimidine, and a phosphate “linker” (Figure 4.11).

In 1944, Avery showed that DNA was able to change one strain of bacteria to another. It is now known that nucleic acids direct the synthesis of proteins. Our modern knowledge of heredity and molecular biology is based on our knowledge of nucleic acids. The decoding of the human genome was declared complete in 2003 but it continues to be defined. This is one of the most important events in the history of humankind to date. The human genome is composed of nature’s most complex, exacting, and important macromolecule. It is composed of nucleic acids that appear complex in comparison to simpler molecules such as methane and ethylene but simple

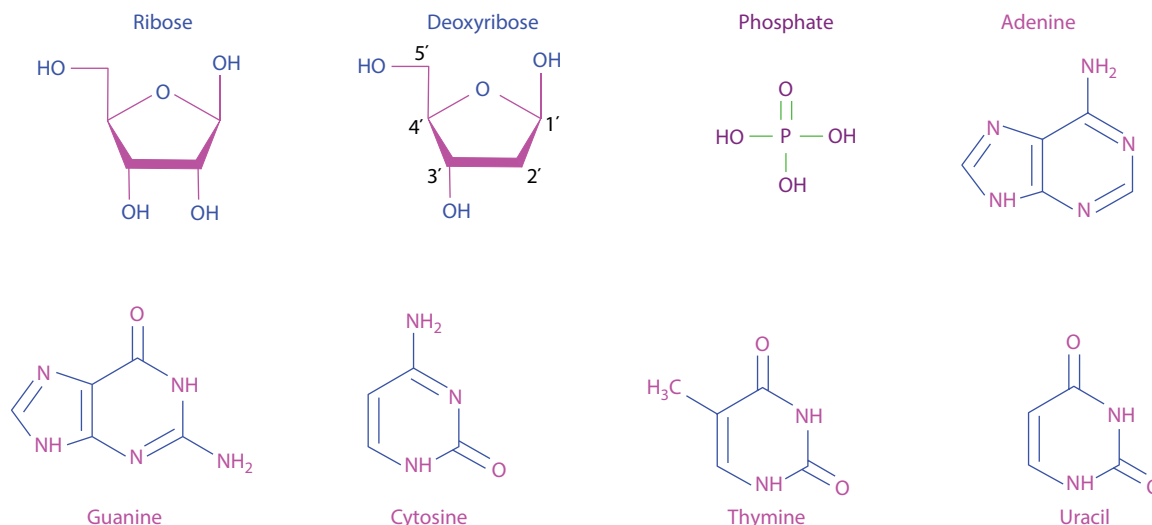
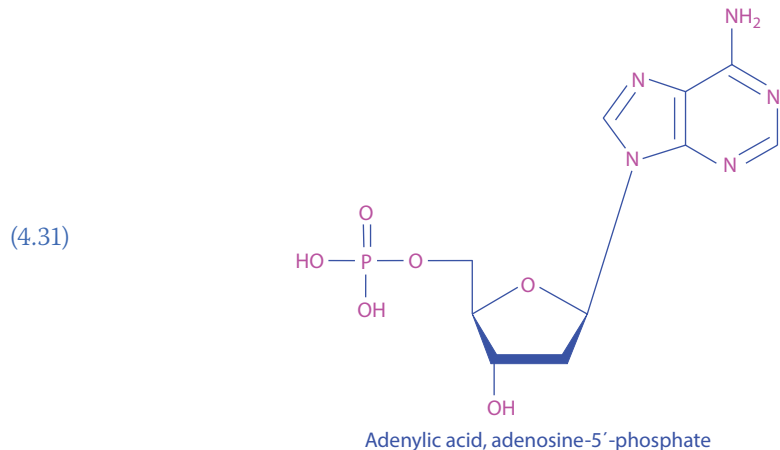


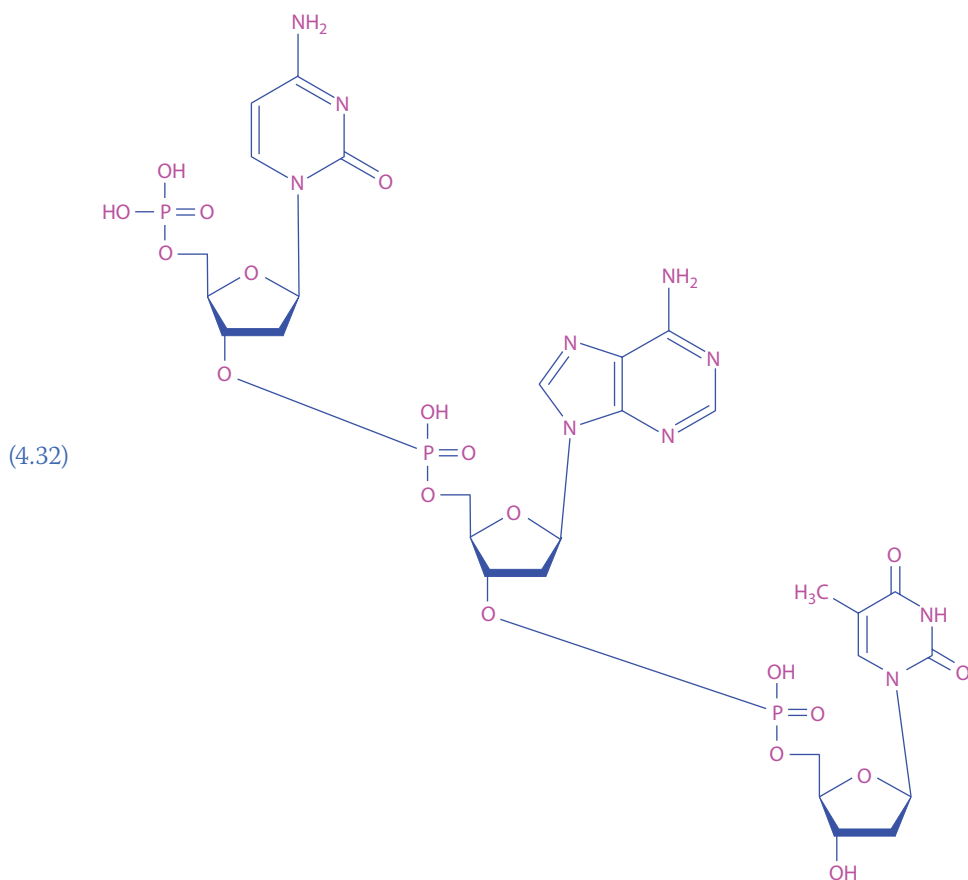
FIGURE 4.11 Components of nucleic acids.

in comparison to their result on the human body. Each unit is essentially the same containing a phosphate and a deoxyribose sugar and one of four bases (Figure 4.11) with each base typically represented by the capital of the first letter of their name, G, C, A, and T. In fact, the complexity is less than having four separate and independent bases because the bases come in matched sets, they are paired. The mimetic Gee CAT allows an easy way to remember this pairing (G-C and A-T). The base, sugar, and phosphate combine forming nucleotides such as adenylic acid, adenosine-5'-phosphate (4.31), and represented by the symbols A, dA, and dAMP.



The backbone of nucleic acids is connected through the 3' and 5' sites on the sugar with the base attached at the 1' site. Because the sugar molecule is not symmetrical, each unit can be connected differently, but there is order (also called sense or directionality) in the sequence of this connection so that phosphodiester linkage between units is between the 3' carbon of one unit and the 5' carbon of the next unit. Thus, nucleic acids consist of units connected so that the repeat unit is a 5'-3' (by agreement, we consider the start to occur at the 5' and end at the 3' though we could just as easily by agreement gone in the opposite direction for our description) linkage. Thus, the two ends are not identical—one contains an unreacted 5'-phosphate and the other an unreacted 3'-unreacted hydroxyl.

A shorthand is used to describe nucleic acid sequences. Following is a trimer containing in order the bases cytosine, adenine, and thymine.



This sequence is described as $p\text{-}5'\text{-C-}3'\text{-p-}5'\text{-A-}3'\text{-p-}5'\text{-T-}3'$ or pCpApT or usually as simply CAT.

Nobel Laureates Watson and Crick correctly deduced that DNA consisted of a double-stranded helix in which a pyrimidine base on one chain or strand was hydrogen bonded to a purine base on the other chain (Figure 4.12). The bonding distances are not the same with the GC pairing more compact. These uneven pairing distances result in a DNA with a characteristic twisting giving unique structures. It is this twisting, and the particular base sequence, that eventually results in the varying chemical and subsequently biological activities for various combinations.

The stability of the DNA is due to both internal and external hydrogen bonding as well as ionic and other bonding. First, the internal hydrogen bonding is between the complementary purine–pyrimidine base pairs. Second, the external hydrogen bonding occurs between

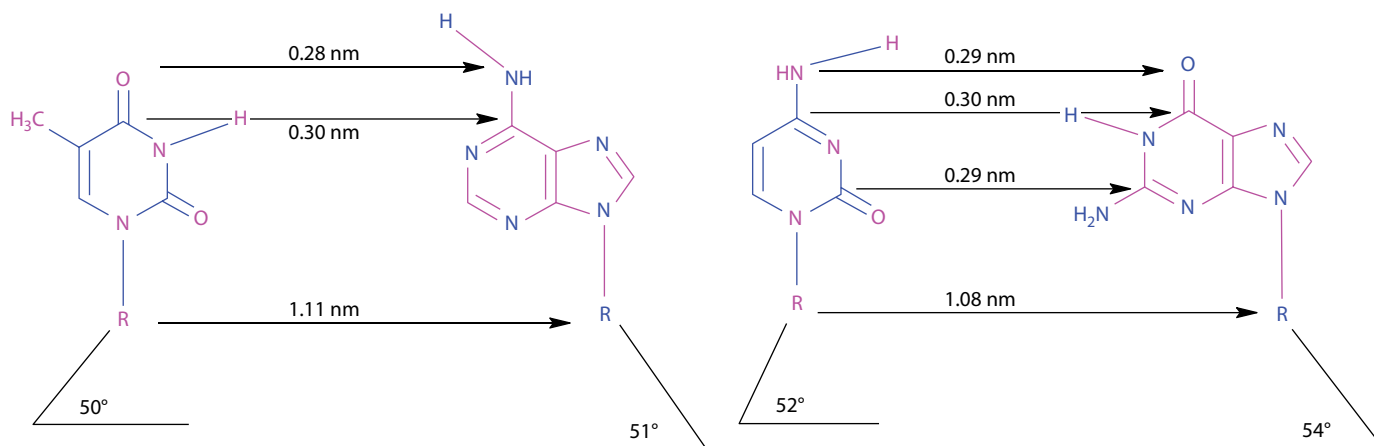


FIGURE 4.12 Hydrogen bonding between preferred base pairs in deoxyribonucleic acid.

the polar sites along exterior sugar and phosphate moieties and water molecules. Third, ionic bonding occurs between the negatively charged phosphate groups situated on the exterior surface of the DNA and electrolyte cations such as Mg^{2+} . Fourth, the core consists of the base pairs, which, along with being hydrogen bonded, stack together through hydrophobic interactions and van der Waals forces. In order to take good advantage of pi-electron cloud interactions, the bases stack with the flat “sides” over one another so that they are approximately perpendicular to the long axis.

The AT and CG base pairs are oriented in such a manner that the sugar-phosphate backbones of the two twined chains are in opposite or antiparallel directions with one end starting at the 5' and ending at the 3', and the starting end of the other across from the 5' end being a 3' end and opposite the other 3' end is a 5' end. Thus, the two chains “run” in opposite directions.

The glucose bonds holding the bases onto the backbone are not directly across the helix from one another. Thus, the sugar-phosphate repeat units are not the same. This dislocation creates structures referred to as major and minor grooves. It is known that at least some proteins that bind to DNA recognize the specific nucleotide sequences by “reading” the hydrogen bonding pattern presented by the edges of these grooves.

In solution, DNA is a dynamic, flexible molecule. It undergoes elastic motions on a nanosecond time scale most closely related to changes in the rotational angles of the bonds within the DNA backbone. The net result of these bendings and twistings is that DNA assumes a roughly globular or spherical tertiary shape. The overall structure of the DNA surface is not that of a reoccurring “barber pole” but rather because of the particular base sequence composition, each sequence will have its own characteristic features of hills, valleys, bumps, etc.

As the two strands in a double helix separate, they act as a template for the construction of a complementary strand. This process occurs enzymatically with each nucleotide being introduced into the growing chain through matching it with its complementary base on the existing chain. Thus, two identical strands are produced when one double-helix combination replicates.

DNA chains can contain 1 million subunits with an end-to-end contour length of about 1 mm. Even with the complexity of these large macromolecules, synthesis of new chains generally occurs without any change in the molecule. Even when changes occur, these giant machines have built into them “correcting” mechanisms that “correct” when mistakes occur.

The transcription product of DNA is always single-stranded RNA. The single strand generally assumes a right-handed helical conformation mainly caused by base-stacking interactions also present in the DNA. The order of interaction is purine–purine \gg purine–pyrimidine $>$ pyrimidine–pyrimidine. The purine–purine interaction is so strong that a pyrimidine separating two purines is often displaced from the stacking order to allow the interaction between the two purines to occur. Base pairing is similar to that of the DNA except that uracil generally replaces thymine. For coupled RNA, the two strands are antiparallel as in DNA. Where complementary sequences are present, the predominant double-stranded structure is an A form right-handed double helix. Many RNAs are combinations of complementary two-stranded helices, single-stranded segments, and other complex structures. Hairpin curves are the most common type of more complex structure in RNA. Specific sequences, such as UUCG, are generally found at the ends of RNA hairpin curves. Such sequences can act as starting points for the folding of an RNA into its precise 3D structure. The tertiary structures for RNAs are complex with combinations being present. For instance, the tertiary structure for the transfer RNA (tRNA) of yeast for phenylalanine consists of a cloverleaf including three loops formed by hairpin curves and double-helix regions stabilized by hydrogen bonding. Hydrogen bonding sites that are not significant in the DNA structures are important because the free hydroxyl on the ribose sugar moiety can hydrogen bond with other units.

There are four major kinds of RNA. Messenger RNA (mRNA) varies greatly in size from about 75 units to over 3,000 nucleotide units giving a molecular weight of 25,000 to 1 million. It is present at a percentage of about 2% of the total RNA in a cell. tRNA has about 73–94 nucleotides with a corresponding molecular weight range of 23,000–30,000. It is present in the cell at a level of about 16%. The most abundant RNA, 82%, is the ribosomal RNA (rRNA) that has several groupings of molecular weight with the major ones being about 35,000 (about 120 nucleotide units), 550,000 (about 1,550 units), and 1,100,000 (about 2,900 units). Eukaryotic cells contain an additional type called small nuclear RNA.

tRNAs contain hairpin curves that promote complementary stretches of base bonding giving regions where helical double stranding occurs. The usual overall structure can be represented as a cloverleaf with each cloverleaf containing four of these helical double-stranded units. One of the loops acts as the acceptor stem that serves as the amino acid—donating moiety in protein synthesis.

rRNA is a part of the protein synthesizing machinery of cells, ribosomes. Ribosomes contain two subunits called “small” and “large” with rRNAs being part of both of these units. rRNAs contain a large amount of intrastrand complementary sequences and are generally highly folded. Interestingly, there is a similarity between the folded structures of rRNA from many different sources even though the primary structure, base sequence, is quite varied. Thus, there appears to be preferred folding patterns for rRNAs.

mRNA is the carrier of messages that are encoded in genes to the sites of protein synthesis in the cell where this message is translated into a polypeptide sequence. Because mRNAs are transcribed copies of the genetic unit, they are sometimes referred to as being the “DNA-like RNA.” mRNA is made during transcription, an enzymatic sequence in which a specific RNA sequence is “copied” from a gene site. rRNA and tRNA are also made by transcription of DNA sequences but unlike mRNA, they are not subsequently translated to form proteins.

Actual reproduction steps involving DNA and RNA often occur in concert with protein where the protein can act as a clamp or vice holding the various important members involved with the particular reproduction step in place. Thus, the protein complex acts as an assembly line tunnel or doughnut with the reactants present within the interior.

There are two types of cells. *Prokaryote cells* lack a cell nucleus or any other membrane-bound organelles. Most organisms possessing prokaryote cells are single celled. Bacteria and archaea are examples of organisms with prokaryote cells. *Eukaryote cells* possess enclosed membranes and form the basis of animals, plants, and fungi. In prokaryote cells, the mRNA can be used immediately after it is produced or it may be bound to a ribosome. In comparison, in eukaryote cells, mRNA is made in the cell nucleus and it can be moved across the nuclear membrane after it is synthesized into the cytoplasm where protein synthesis occurs.

4.8.2 FLOW OF BIOLOGICAL INFORMATION

Nucleic acids, proteins, some carbohydrates, and hormones are informational molecules. They carry directions for the control of biological processes. With the exception of hormones, these are macromolecules. In all these interactions, secondary forces such as hydrogen bonding and van der Waals forces, and ionic bonds and hydrophobic/hydrophilic character play critical roles. *Molecular recognition* is the term used to describe the ability of molecules to recognize and interact (bond) specifically with other molecules. This molecular recognition is based on a combination of these interactions just cited and on structure.

Molecular recognition interactions have several common characteristics. First, the forces that are involved in these interactions are relatively weak and they are noncovalent. They are on the order of about 1–8 kcal/mol (4–30 kJ/mol) compared to covalent bonds of the order of about 80 kcal/mol (300 kJ/mol) for a C–C sigma bond. A single secondary bond is generally not capable of holding molecules together for any length of time. But for macromolecules, there is a cumulative effect so that the forces are not singular but are multiplied by the number of such interactions that are occurring within the particular domain. Second, these interactions are reversible. Initial contact occurs as the molecules come into contact with one another often through simple diffusion or movement of the molecules or segments of the molecules. These initial contacts are often not sufficient to cause the needed binding though some transitory interactions occur. Even so, in some cases, the cumulative bonding is sufficient to allow a transient but significant interaction to occur. This complex can then begin a specific biological process. Eventually, thermal motions and geometrical changes cause the complex to dissociate. Ready reversibility is an important key that allows a relatively few “signaling” molecules to carry out their mission. Third, bonding between the particular molecular sites is specific. There must exist a combination of complementary bonding, hydrophobic/hydrophilic sites, ionic charge, and geometry that allow effective long-term (generally no more than several seconds) interactions to occur.

In general, the flow of biological information can be mapped as follows:

(4.33) DNA → RNA → Protein → Cell structure and function

The total genetic information for each cell, called the “**genome**,” exists in the coded two-stranded DNA. This genetic information is expressed or processed either through duplication of the DNA so it can be transferred during cell division to a daughter cell or it can be transferred to mRNA that in turn transfers the information to proteins that carry out the activities of the cell.

Duplication of double-stranded DNA is self-directed. The DNA, along with accessory proteins, directs the **replication** or construction of two complementary strands forming a new, exact replicate of the original DNA template. As each base site on the DNA becomes available through the unraveling of the double-stranded helix, a new nucleotide is brought into the process held in place by hydrogen bonding and van der Waals forces so that the bases are complementary. It is then covalently bonded through the action of an enzyme called DNA polymerase. After duplication, each DNA contains one DNA strand from the original double-stranded helix and one newly formed DNA strand. This is called “**semiconservative replication**” and increases the chance that if an error occurs, the original base sequence will be retained.

How is DNA suitable as a carrier of genetic information? While we do not entirely understand, several features are present in DNA. First, because of the double-stranded nature and mode of replication, retention is enhanced. Second, DNA is particularly stable within both cellular and extracellular environments, including a good stability to hydrolysis within an aqueous environment. Plant and animal DNA have survived thousands of years. Using polymerase chain reactions (PCRs), we can reconstruct DNA segments allowing comparisons to modern DNA.

Transcription is the term used to describe the transfer of information from the DNA to RNA. The genome is quite large, on the order of a millimeter in length if unraveled, but within it exists coding regions called genes. Transcription is similar to DNA replication except ribonucleotides are the building units instead of deoxyribonucleotides; the base thymine is replaced by uracil; the DNA:RNA duplex unravels releasing the DNA to again form its double-stranded helix and the single-stranded RNA; and the enzyme linking the ribonucleotides together is called RNA polymerase.

Many viruses and retroviruses have genomes that are single-stranded RNA instead of DNA. These include the AIDS virus and some retroviruses that cause cancer. Here, an enzyme called reverse transcriptase converts the RNA genome of the virus into the DNA of the host cell genome thus infecting the host.

The transcription of the DNA gives three kinds of RNA—ribosomal, messenger, and transfer. The most abundant RNA is rRNA. Most rRNA is large and is found in combination with proteins in the ribonucleoprotein complexes called ribosomes. Ribosomes are subcellular sites for protein synthesis.

tRNA is the smallest of the RNAs being less than 100 nucleotides long. tRNA combines with an amino acid incorporating it into a growing protein. There is at least one tRNA for each of the 20 amino acids used in protein synthesis. mRNA is varied in size but each carries the message found in a single gene or group of genes. The sequence of bases in mRNA is complementary to the sequence of DNA bases. mRNA is unstable and short-lived so that its message for protein synthesis must be rapidly decoded. The message is decoded by the ribosomes that make several copies of the protein for each mRNA.

The ultimate purpose of DNA expression is protein synthesis. mRNA serves as the intermediate carrier of the DNA genetic information for protein synthesis. The DNA message is carried in the form of base sequences that are transferred to RNA also in terms of base sequences, and finally, these are transferred into amino acid sequences through a translation process based on the genetic code. This process of information from the RNA to the protein is called “**translation**.”

A set of coding rules are in action as in the translation process. Briefly, these are as follows. First, a set of three adjacent nucleotides compose the code for each amino acid. A single amino acid can have several triplet codes or **codons**. Since there are four different nucleotides (or four different bases) in DNA and RNA, there exists 4^3 or 64 trinucleotide combinations. For instance, using U as a symbol for uracil, present in RNA, the triplet or code or codon UUU is specific for phenylalanine.

Second, the code is nonoverlapping so that every three nucleotides code for an amino acid and the next three code for a second amino acid and the third set code for a third amino acid, etc. Third, the sets of nucleotides are read sequentially without punctuation. Fourth, the code is nearly universal. Fifth, there are codes for other than amino acids including stop or terminate, UAG, and start or initiate, AUG.

In essence, tRNA has two active sites—one that is specific for a given amino acid and the second that is specific for a given set of three bases. The tRNA “collects” an appropriate amino acid and brings it to the growing polypeptide chain inserting it as directed by the mRNA. There is then a collinear relationship between the nucleotide base sequence of a gene and the amino acid sequence in the protein.

The amount, presence, or absence of a particular protein is generally controlled by the DNA in the cell. Protein synthesis can be signaled external to the cell or within the cell. Growth factors and hormones form part of this secondary messenger service.

The translation and transcription of DNA information is polymer synthesis and behavior, and the particular governing factors and features that control these reactions are present in the synthesis and behavior of other macromolecules—synthetic and biological.

For the human genome, there exists the so-called coding or active regions called “**exons**” and noncoding regions called “**introns**.” The average size of an exon is about 120–150 nucleotide units long or coding for about 40–50 amino acids. Introns vary widely in size from about 50 to over 20,000 units. About 5% of the genome is used for coding. It was thought that the other 95% was silent or junk DNA. We are finding that the introns play essential roles. Interestingly, introns are absent in the most basic prokaryotes, only occasionally found in eukaryotes, but common in animals.

Protein synthesis occurs on the average of two amino acid units every second.

4.8.3 NEXT STEPS

Materials act in three dimensions. We have long realized that polymers gain most of their physical properties from their 3D structures. Recently, we are finding out how critical the 3D structures of natural materials are. Such 3D structures are critical for gene regulators.

The next step in the journey to uncover “what makes us tick” has begun emerging. ENCODE is the name given to the most recent project. Some of the findings are initially unexpected, but not as unexpected after consideration. This study group described a list of genes and locations along the DNA strands. These sites include locations where proteins attach to the DNA to control genes or where enzymes connect making seeming small changes.

Initially, most of the DNA was considered “junk” or inactive domains where, at best, the DNA provided contour for active sites to properly function. The new analyses show that greater than 80% of the human DNA is active in at least one biological process. Many of the new sites are regulators dictating whether instructions carried by a gene to synthesize a protein will be executed. This regulation is a major key since each cell in our body contains the complete set of about 21,000 protein-making genes. To adapt to its identity, each cell needs to activate only one subset of them.

These regulators or switches turn off and on genes at various times and intensities. Some of these switches are near the particular gene they help regulate while others are well removed. This is one of the unexpected findings. But this finding may not be as unexpected as initially thought. We generally think of DNA as existing in a long stringlike arrangement but in truth, it is tightly folded and compacted in the cell so that adjoining segments of the DNA string might lay adjacent to one another—the to-be-activated gene and the activating switch/regulator.

Knowledge of the switches should allow a better understanding of which certain combinations of DNA variants may increase the chances for a particular disease. With respect to many diseases, it is found that the variants associated with the diseases generally are located in sites involved in regulation of the gene.

The 2012 Nobel Prize in Chemistry was awarded to Robert Lefkowitz and Brian Kobilka for figuring out the molecular workings of G-protein-coupled receptors (GPCRs). These receptors are a family of proteins that transmit biological messages for functions such as neurotransmission,

smell, vision, and taste. GPCRs regulate most of the physiological processes in us. We have known for some time that hormones outside the cells caused changes within the cells, but the means of sending these signals was not known. Kobilka isolated a gene encoding protein for the beta-adrenergic receptor in the 1980s and found that it was composed of seven helices. Kobilka and Lefkowitz believed that this was one member of a group of seven helical proteins that acted as critical receptors. They were correct.

The GPCRs are the targets of many drugs, possibly one-half of the pharmaceuticals used today including beta-blockers for control of high blood pressure. In fact, some recent emphasis has focused on the synthesis of possible drugs based on the structures of natural hormones with the additional purpose of avoiding side effects.

A nice article describing some of the changing technology involving genomics and the ability to treat genetic diseases is given in “Genome Editing WRIT Large” (C&EN, Washington, DC, September 7, 2015, pp. 14–20).

4.9 NATURALLY OCCURRING POLYISOPRENES AND OTHER SYNTHETIC ELASTOMERS

Polyisoprenes occur in nature as hard plastics called gutta-percha and balata and as an elastomer or rubber known as *Hevea brasiliensis*, or natural rubber (NR). Approximately 50% of the 500 tons of gutta-percha produced annually is produced from trees grown on plantations in Java and Malaya. Balata and about 50% of the gutta-percha used are obtained from trees in the jungles of South America and the East Indies. The first gutta-insulated submarine cable was installed between England and France in 1859. Gutta-percha (*Palaquium oblongifolium*) continues to be used for wire insulation and polyisoprene, balata (*Mimusops globosa*), and gutta-percha are used as covers for some golf balls.



The hardness of some of the polydisperse naturally occurring crystalline polymers is the result of a *trans* configuration in 1,4-polyisoprene (Figures 4.13 and 4.14). This geometry facilitates good

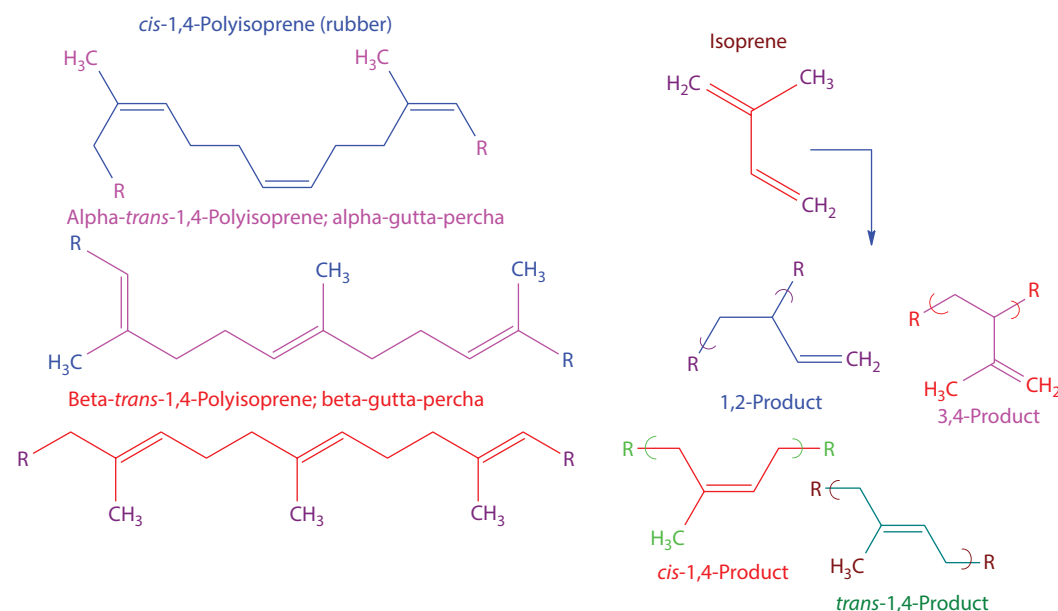


FIGURE 4.13 Abbreviated structural formulas for polyisoprenes.

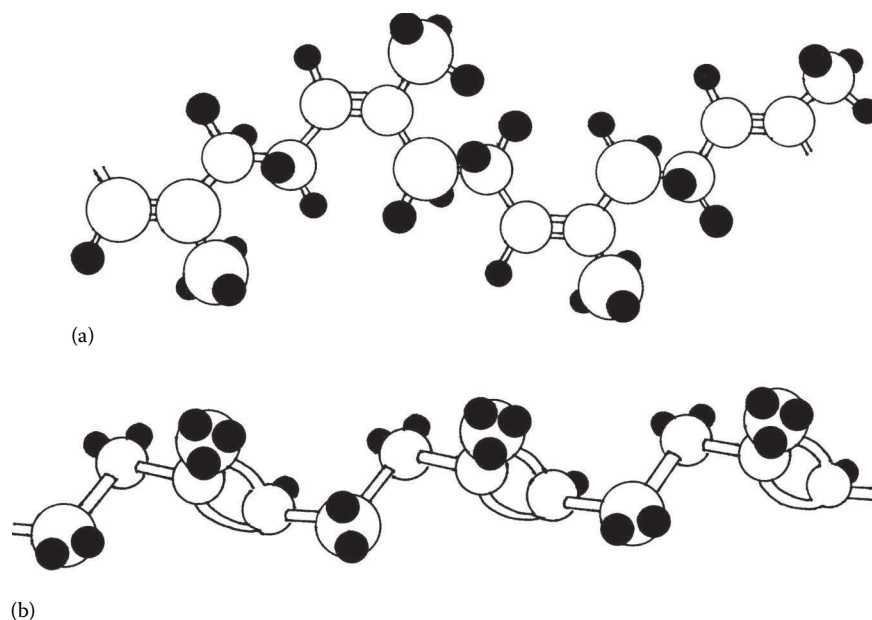


FIGURE 4.14 Ball-and-stick models of (a) “soft” *Hevea* rubber (*cis*-1,4-polyisoprene) and (b) “hard” gutta-percha (*trans*-1,4-polyisoprene).

fit between chains and results in inflexibility in the chains. The *Hevea* or NR is, by comparison, soft because it is a *cis* configuration (Figures 4.13 and 4.14) that does not allow a close fit between chains resulting in flexibility and a “rubbery” behavior. Both *trans* and *cis* isomers of polyisoprene are present in chicle, obtained from the *Achras sapota* tree in Central America. Both *trans* and *cis* isomers are also synthesized commercially.

There exist related observations associated with fatty acids. Cold-blooded animals such as lizards and snakes have a higher proportion of unsaturated fats compared to warm-blooded animals. Further, the unsaturation is generally of the *cis* variety. As in the case of *Hevea* rubber, the *cis* configurations encourage the fatty acid chains to be further apart. This lessens the formation of tightly fitted chains allowing them to be fluid at lower temperatures. By comparison, warm-blooded animals furnish their own energy to maintain body temperature so the importance of unsaturation and the type of unsaturation are less critical for their survival. The presence of the unsaturated and trans-saturation for warm-blooded animals allows for more tightly fitted cell walls that are less porous in comparison to cold-blooded animals.

NR was used by the Mayan civilization in Central and South America before the twentieth century. In addition to using the latex from the ule tree for waterproofing of clothing, they played a game called “tlachtli” with large *Hevea* rubber balls. The object of the game was to insert the ball into a tight-fitting stone hole in a vertical wall using only the shoulder or thigh. The game ended once a goal was scored, and the members of the losing team could be sacrificed to the gods.

While NR or caoutchouc was brought to Europe by Columbus, little use beyond erasing pencil marks was made of this important elastomer until the nineteenth century. Priestly coined the name India rubber to describe its major use at that time. *Hevea* latex is also present in many other plants in addition to *H. brasiliensis*. There has been interest in growing some of these plants and harvesting the NR but thus far, other than the guayule, none have become commercial-scale enterprises.

Charles Goodyear was born in 1800 in New Haven Connecticut. He became driven to work with rubber to try to make it more temperature stable. This passion affected his health and took what little money he had. On more than one occasion, he lived in debtor’s prison. One of his jobs was to supply the U.S. government with waterproof mailbags, but the mailbags he prepared were sticky and malformed, another failure. After many unsuccessful attempts, one of which was to mix the rubber with sulfur, he accidentally allowed a mixture of sulfur and rubber to touch a

hot stove. The rubber did not melt but only charred a little. As are many of the so-called discoveries by chance or accident, his mind was ready for the result and by 1844 had been given a patent for a process he called “vulcanization” after the Roman god of fire, Vulcan. Vulcanization is the cross-linking reaction between the rubber chains and the sulfur.

Goodyear had trouble defending his patent, piling up huge debts before he died in 1860. Daniel Webster defended him in one of his patent infringement cases. By 1858, the value of rubber goods was about \$5 million. The major rubber producing plants clustered about Akron, Ohio, with the Goodyear Company founded in 1870.

While most “rubbery” products are made from synthetic rubber (SR), rubber bands (Picture 4.19) are made from NR because of its better elasticity.

Chemists learned about the structure of rubber by degrading it through heating and analyzing the evolved products. One of the evolved products was isoprene, a five carbon hydrocarbon containing a double bond. Isoprene is a basic building block in nature serving as the “repeat” unit in rubber and also the building block of steroids such as cholesterol.



With knowledge that NR had isoprene units, chemists worked to duplicate the synthesis of rubber except using synthetic monomers. These attempts failed until two factors were realized. First, after much effort, it was discovered that the methyl groups were present in a “*cis*” arrangement. Second, it was not until the discovery of stereoregular catalysts that the chemists had the ability to form NR-like material from butadiene.

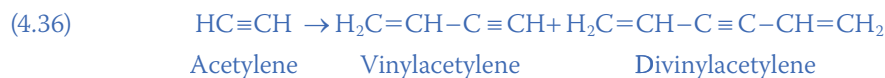
The synthesis of a purely synthetic rubber, SR, structurally similar to NR, involved a number of scientists building upon one another’s work—along with a little creativity. Nieuwland, a Catholic priest, President of Notre Dame University, and a chemist, did extensive work on acetylene. He found that acetylene could be made to add to itself forming dimers and trimers.

Calcott, a DuPont chemist, attempted to make polymers from acetylene, reasoning that if acetylene formed dimers and trimers, conditions could be found to produce polymers. He failed, but went to Carothers who had one of his chemists, Arnold Collins, work on the project. Collins ran the reaction described by Nieuwland, purifying the reaction mixture. He found a small amount of material that was not vinylacetylene or divinylacetylene (4.36). He set the liquid aside.

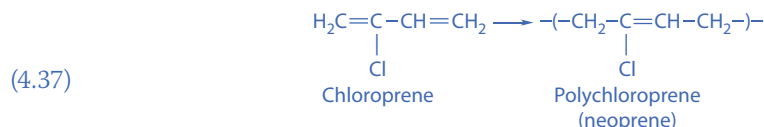


PICTURE 4.19 Rubber bands—an assortment of colors and dimensions.

When he came back, the liquid had solidified giving a material that seemed rubbery and even bounced. They analyzed the rubbery material and found that it was not a hydrocarbon, but it had chlorine in it. The chlorine had come from HCl that was used in Nieuwland's procedure to make the dimers and trimers adding to the vinylacetylene forming chloroprene (4.37).



This new rubber was given the name Neoprene (4.37). Neoprene had outstanding resistance to gasoline, ozone, and oil in contrast to NR. Today, Neoprene is used in a variety of applications including electrical cable jacketing, window gaskets, shoe soles, industrial hose, and heavy duty drive belts.



Prior to the discovery of the vulcanization or cross-linking of *Hevea* rubber with sulfur by Charles Goodyear in 1838, Faraday has shown that the empirical formula of this elastomer is C_5H_8 making it a member of the terpene family. The product obtained by pyrolysis of rubber was named isoprene by Williams in 1860 and it was converted to a solid (polymerized) by Bouchardat in 1879.

NR crystallized when stretched in a reversible process. However, the sample remains in its stretched form (racked rubber) if it is cooled below its T_g . The racked rubber will snap back and approach its original form when it is heated above its T_g . The delay in returning to the original form is called "hysteresis." These and other elastic properties of NR and other elastomers above the T_g are based on long-range elasticity. Stretching causes an uncoiling of the polymer chains, but these chains assume a more ordered microstructure creating crystalline domains acting to oppose further stretching. If the rubber is held in the stretched state for some time, slippage of chains occurs and precise return to its original shape does not occur when the stress is released.

The absence of strong intermolecular forces, presence of pendant methyl groups discouraging close association, and crankshaft action associated with the *cis* isomer all contribute to the flexibility of NR. The introduction of a few cross-links by vulcanization with sulfur reduces slippage of chains but still permits good flexibility.

When a strip of NR or SR is stretched at a constant rate, the tensile strength required for stretching (stress, s) increases slowly until elongation (strain) of several hundred percent is observed. This initial process is associated with an uncoiling of the polymer chains in the uncross-linked regions. Considerably, more stress is required for greater elongation to about 800%. This rapid increase in modulus (G) is associated with better alignment of the polymer chains along the axis of elongation, crystallization, and decrease in entropy (ΔS). The work done in the stretching process (W_1) is equal to the product of the retractile force (f) and the change in length (dl). Therefore, the force is equal to the work per change in length:

$$(4.38) \quad W_1 = f \, dl \quad \text{or} \quad f = \frac{W_1}{dl}$$

W_1 is equal to the change in Gibbs free energy (dG), which under the conditions of constant pressure is equal to the change in internal energy (dE) minus the product of the change in entropy and the Kelvin temperature as follows:

$$(4.39) \quad f = \frac{W_1}{dl} = \frac{dG}{dl} = \frac{dE}{dl} - T \left(\frac{dS}{dl} \right)$$

The term (dE/dl) in this equation is important in the initial low-modulus stretching process, and the next term $[T(dS/dl)]$ predominates in the second high-modulus stretching process. For an ideal rubber, only the second of these two terms is involved.

As observed by Gough in 1805 and verified by Joule in 1859, the temperature of rubber increases as it is stretched, and the stretched sample cools as it snaps back to its original condition. (This can be easily confirmed by you by rapidly stretching a rubber band and placing it to your lips, noting that heating has occurred, and then rapidly releasing the tension and again placing the rubber band to your lips.) This effect was expressed mathematically by Kelvin and Clausius in the 1850s. The ratio of the rate of change of the retractive force (df) to the change in Kelvin temperature (dT) in an adiabatic process is equal to the specific heat of the elastomer (C_p) per degree temperature (T) times the change in temperature (dT) times the change in length (dl):

$$(4.40) \quad \frac{df}{dT} = -\left(\frac{C_p}{T}\right)\left(\frac{dT}{dl}\right)$$

Equation 4.40 may be transformed to the following equation:

$$(4.41) \quad \frac{dT}{df} = -\left(\frac{T}{C_p}\right)\left(\frac{dl}{dT}\right)$$

Unlike most solids, NR and other elastomers contract when heated. As we have noted before, for most materials to be elastic, the prestretched state is high in disorder compared to the stretched material. Thus, the change in entropy or order when stretched goes against the natural tendency so that the driving force to return to its prestretched form is due to entropy rather than enthalpy related. We generally want the applied force to be small to bring about elongation of the rubber. Most “good” elastomers are composed of mainly hydrocarbon units that are held together with low-energy secondary forces, namely, dispersion forces. In truth, the energies of the hydrocarbon units in the two states, stretched and nonstretched, are essentially the same, dispersion forces. The energy needed to produce the “stretch” is used to cause conformational changes resulting in an uncoiling for the rubber in its relaxed, unstretched state and formation of crystalline portions that act as sites of cross-linking resisting further elongation. These conformational changes require two things—available space and added energy. As we noted earlier, elastomers contract when heated. Further, the rubbery material becomes warm as it is stretched. The work required to stretch the rubber is not retained by the stretched elastomers but rather is released as heat.

4.9.1 BALLOONS

Balloons have been part of our everyday lives from birth to graduations. As with many simple objects, their origin is unknown. Balloon-like objects have been part of ancient stories and probably were initially used in sports. These early balloons were made of animal bladders and intestines, both being protein based and hence polymeric. European jesters inflated the animal entrails using them to entertain others. Galileo inflated a pig’s bladder to help measure the weight of air.

While there are also new world mentions of similar balloon construction, it was not until rubber arrived on the scene that the manufacture of balloons, as balloons we know today, began.

In 1824, Michael Faraday used NR to produce balloons for his hydrogen experiments at the Royal Institution in London. He writes, “...The caoutchouc is exceedingly elastic....Bags made of it... have been expanded by having air forced into them, until the caoutchouc was quite transparent, and when expanded by hydrogen they were so light as to form balloons with considerable ascending power...” Faraday constructed his balloons by cutting two layered sheets of rubber and then pressing the edges together. Flour was applied to the inside of the balloons because the native rubber was tacky and would adhere preventing it from being inflated.

Toy balloons were introduced by Thomas Hancock in 1825 as a do-it-yourself kit that consisted of a rubber solution and a syringe. Vulcanized toy balloons were initially manufactured

by J.G. Ingram of London in 1847. The vulcanizing caused the balloons to be nontacky and not susceptible to becoming excessively sticky on hot days. Montgomery Ward had balloons in their catalog by 1889.

In America, the story of the balloon coincided with the story of the tire, both requiring an understanding and use of rubber. The initial manufacture of balloons in the United States was in 1907 by the Anderson Rubber Company in Akron, Ohio. In 1912, Harry Rose Gill, founder of the National Latex Rubber Products of Ashland, Ohio, made a nonspherical cigar-shaped balloon. Gill also began packaging balloons in packs, the initial sanitary balloon package.

Neil Tillotson, at 16, began work at the Hood Rubber Company in Boston. After a 2-year period in the Seventh Cavalry during World War I, he returned to the Hood Rubber Company. Of about 25 Hood chemists, Neil was the only one without a college degree. But he was inventive and with the first load of raw rubber latex in the 1920s, he started a life-long romance with rubber. The company's initial efforts with the raw latex were unsuccessful and the company largely dropped its efforts to produce balloons. Tillotson persevered working out of his own home. Eventually, he managed to "tame" the latex sufficiently to make stylistic balloons using techniques similar to what is employed today. They cut a catlike face from cardboard. He dipped the catlike mold in latex and allowed it to dry. Inflated, it did resemble a cat. His first sale was an order for 15 gross for use at the annual Patriots Day Parade on April 19, 1931. Next, he formed a family business, incorporating later in 1931, using his family as an assembly line in the production of balloons. During the great depression, Neil traveled by bus around the country to sell his balloons. The Tillotson Rubber Company is still in operation with the balloon division named Dipco, a nice reminder of the way balloons are still made.

Rubber latex is sensitive to the influence of external forces or chemical agents. Thus, the so-called alligator balloon is formed when solid-colored balloons are dipped in an acid bath causing the balloon to turn into two shades, supposedly like an alligator. The radium balloon is produced by taking a solid-colored balloon and dipping it a second time into another color.

Commercially inflated balloons held hydrogen and helium. Hydrogen was preferred because of its somewhat, about 10%, greater lifting ability. Hydrogen balloons were first produced by Faraday, as noted before. But along with its greater lifting power, hydrogen offers a danger. On ignition, hydrogen burns rapidly forming water and energy, generally producing a fire. As early as 1914, firemen tried to curtail the use of hydrogen-filled balloons. In 1922, New York City banned the use of hydrogen-filled balloons because a city official was badly burned because of a fire caused by hydrogen-filled balloons.

There is an experiment that is often used in polymer demonstrations. Pointed objects such as long pins and sticks are gently pushed into a blow-up balloon without exploding the balloon. This results because the rubber polymer chains form about the impacting object to seal up the "hole" created by the object. Thus, even in its seemingly solid state, the rubber balloon's polymer chains are sufficiently mobile to allow it to "heal" itself.

Balloons today are still made from the rubber latex from the rubber tree using molds. Color is added as desired.

Foil balloons are derived from the effort of NASA Space Command with the concept and technology to metalize plastic sheeting (Picture 4.20). While the balloons are often referred to as Mylar or silver Mylars, they are not made from Mylar, a trade name for certain polyester film. They should be referred to as simply foil balloons. They are made from nylon film coated on one side with polyethylene and metallized on the other. The nylon film gives the balloon some strength, and the polyethylene gives it some flexibility and helps retard the release of the held gas.

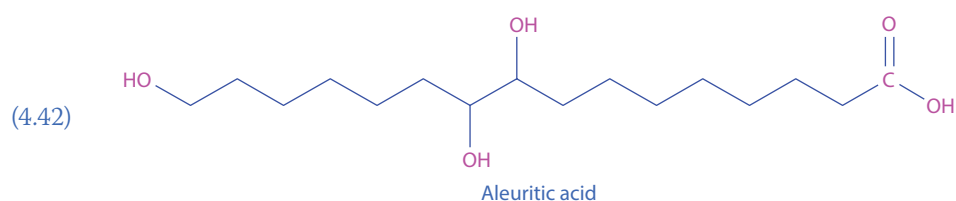
4.9.2 RESINS

Shellac, which was used by Edison for molding his first photograph records and is still used as an alcoholic solution (spirit varnish) for coating wood, is a cross-linked polymer consisting largely of derivatives of aleuritic acid (9,10,16-triphydroxyhexadecanoic acid; 4.42). Shellac is excreted by



PICTURE 4.20 Mylar balloons being sold near Valentine's Day.

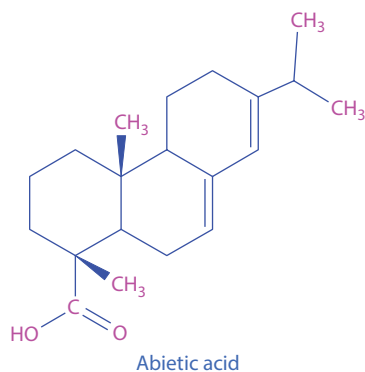
small coccid insects (*Coccus lacca*) that feed on the twigs of trees in Southeast Asia. More than 2 million insects must be dissolved in ethanol to produce 1 kg of shellac.



4.9.3 ROSIN AND RELATED MATERIALS

Rosin, the residue left in the manufacture of turpentine by distillation, is a mixture of the diterpene, abietic acid (4.43), and its anhydride. It is nonpolymeric but is used in the manufacture of synthetic resins and varnishes. Easter gum, a cross-linked ester, is obtained by the esterification of glycerol or pentaerythritol with rosin. Many natural resins are fossil resins exuded from trees thousands of years ago. Recent exudates are called recent resins, and those obtained from dead trees are called semifossil resins. *Humic acid* is a fossil resin found with peat, coal, or lignite deposits throughout the world. It is used as a soil conditioner, as a component of oil-drilling muds, and as a scavenger for heavy metals. Amber is a fossil resin found in the Baltic Sea regions, and sandarac and copals are found in Morocco and Oceania, respectively. *Casein*, a protein from milk, under the name of Galalith, has been used as a molding resin and as an adhesive.

(4.43)



4.10 LIGNIN

Lignin is the second most widely produced organic material, after the saccharides. It is found in essentially all living plants and is the major noncellulosic constituent of wood. It is produced at an annual rate of about 2×10^{10} tons with the biosphere containing a total of about 3×10^{11} tons. It contains a variety of structural units including those pictured in Figure 4.15.

Lignin has a complex structure that varies with the source, growing conditions, etc. This complex and varied structure is typical of many plant-derived macromolecules. Lignin is generally considered as being formed from three different phenylpropanoid alcohols—coniferyl, coumaryl,

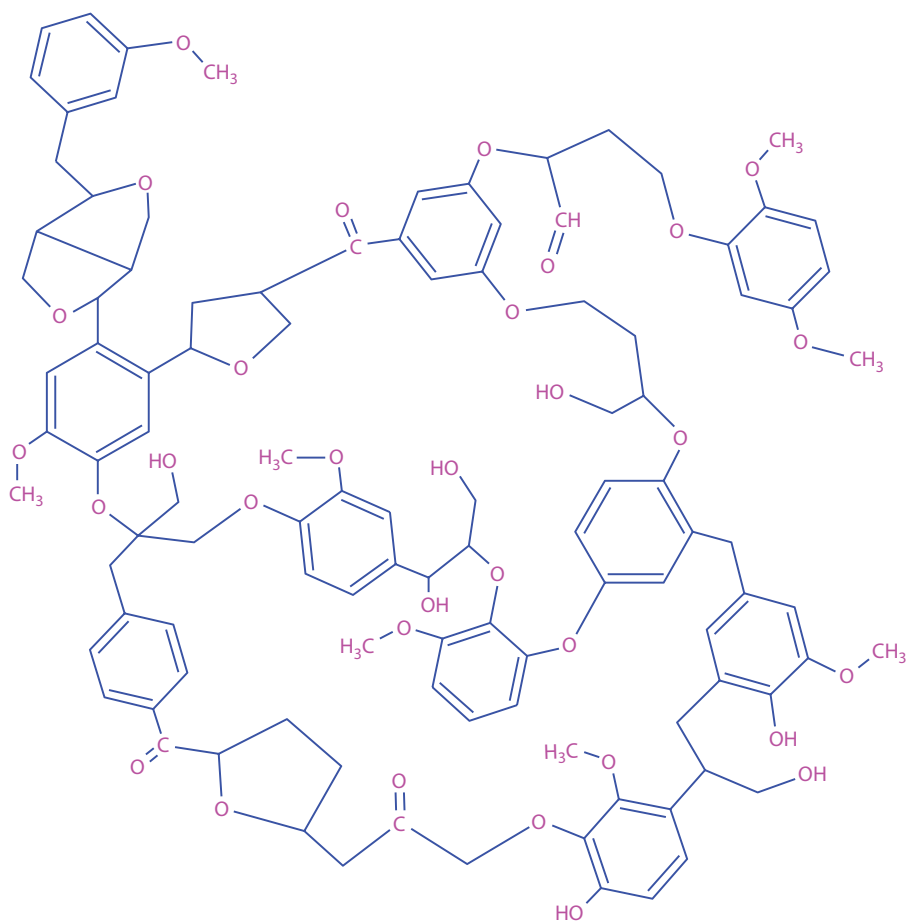


FIGURE 4.15 (Representative) Structure of lignin.

and sinapyl alcohols that are synthesized from phenylalanine via various cinnamic acid derivatives and commercially is sometimes treated as being composed of a C_9 repeat unit where the superstructure contains aromatic and aliphatic alcohols and ethers, and aliphatic aldehydes and vinyl units.

Lignin is found in plant cell walls of supporting and conducting tissue, mostly the tracheids and vessel parts of the xylem. It is largely found in the thickened secondary wall but can occur elsewhere close to the celluloses and hemicelluloses.

The presence of rigid aromatic groups and hydrogen bonding by the alcohol, aldehyde, and ether groups gives a fairly rigid material that strengthens stems and vascular tissue in plants allowing upward growth. It also allows water and minerals to be conducted through the xylem under negative pressure without collapse of the plant. This structure can be flexibilized through introduction of a plasticizer, in nature mainly water. The presence of the hydrophilic aromatic groups helps ward off excessive amounts of water allowing the material to have a variable flexibility but to maintain some strength. This type of balance between flexibility and strength is also utilized by polymer chemists as they work to modify lignin as well as synthetic polymers to give strong, semiflexible materials. Without the presence of water, lignin is brittle but with the presence of water, the tough lignin provides plants with some degree of protection from animals.

Its chemical durability also makes it indigestible to plant eaters and its bonding to cellulose and protein material in the plant also discourages plant eaters from eating it. Formation of lignin also helps block the growth of pathogens and is often the response to partial plant destruction.

The role of transferring water by lignin makes the ability to produce lignin critical to any plant's survival and permits even primitive plants to colonize dry land.

During the synthesis of plant cell walls, polysaccharides are generally initially laid down. This is followed by the biosynthesis of lignin that fills the spaces between the polysaccharide fibers acting to cement them together. The filling of cell wall spaces results in at least some of the lignin having a somewhat 2D structure similar to a sheet of paper rather than the typical 3D structure for most polysaccharides and other natural macromolecules. The lignin sheets act as a barrier toward the outside elements including marauding pests as noted earlier.

The lignin is generally considered as being insoluble but it can be solubilized utilizing special systems such as strong basic solutions that disrupt the internal hydrogen bonding. It is not clear even now if the undegraded lignin is solubilized or if degradation accompanies lignin solubility. Weight average molecular weights for some lignin samples vary depending on the type of solvent employed consistent with degradation occurring for at least some of these systems. Molecular weight values to about 10^7 have been reported for some alkali-extracted fractions.

Solubilized lignin solutions are easily oxidized and the presence of the aromatic units containing electron-donating ether and alcohol moieties makes it available for electrophilic substitution reactions such as nitration, halogenation, and hydroxylation.

Since its removal is the major step in the production of paper pulp, vast amounts of lignin are available as a by-product of paper manufacture. Its industrial use is just beginning and it remains one of the major underused materials. Its sulfonic acid derivative is used as an extender for phenolic resins, as a wetting agent for oil-drilling muds, and for the production of vanillin. Combined, this accounts for less than 1% of this important "by-product." In the enlightened age of green chemistry, greater emphasis on the use of lignin itself and in products derived from it must occur.

4.11 MELANINS

Light is continuous ranging from wavelengths smaller than 10^{-12} cm (Gamma Radiation) to greater than 10^8 cm. Radiation serves as the basis for the synthesis of many natural macromolecules via photosynthesis. Radiation is used commercially to increase the wood pulp yield through cross-linking and grafting of lignin and other wood components onto cellulosic chains. Radiation is also used in the synthesis and cross-linking of many synthetic polymers.

Radiation is also important in the synthesis and rearrangement of important “surface” macromolecules. Tanning of human skin involves the activation of the polypeptide hormone beta-MSH that in turn eventually leads to the phenomena of tanning. Exposure to higher-energy light from about 297 to 315 nm results in both tanning and burning, whereas exposure to light within the 315–330 nm region results in mainly only tanning.

UV radiation activates enzymes that modify the amino acid tyrosine in pigment-producing cells, the melanocytes. The enzyme tyrosinase, a copper-containing oxygenase, catalyzes the initial step that is the hydroxylation of tyrosine to 3,4-dihydroxyphenylalanine that is oxidized to dopaquinone subsequently forming the melanins (Figure 4.16). The concentration of tyrosine is relatively high in skin protein. These modified tyrosine molecules undergo condensation forming macromolecules known as melanins. Melanins have extended chain resonance where the pi electrons are associated with the growing melamine structure. As the melamine structure grows, it becomes more colored giving various shades of brown color to our skin. This brown coloration acts to help protect deeper skin elements from being damaged by the UV radiation. The absence of the enzyme tyrosinase that converts tyrosine to melanin can lead to albinism.

At least two colored melanins are formed—a series of black melanins and a series of the so-called red melanins. Our skin pigmentation is determined by the relative amounts of these red and black melanins in our skin.

The concentration of melanin also contributes to the color of our hair (except for redheads where the iron-rich pigment trichosiderin dominates). The bleaching of hair, generally achieved through exposure to hydrogen peroxide, is a partial result of the oxidation of the melanin. A side reaction of bleaching is the formation of more sulfur cross-links leading to bleached hair being more brittle because of the increased cross-linking leading to a decrease in hair flexibility.

Melanin also provides a dark background in our eye's iris, is involved in animal color changes (such as the octopus and chameleon), is formed when fruit is bruised, and is partially responsible for the coloration of tea.

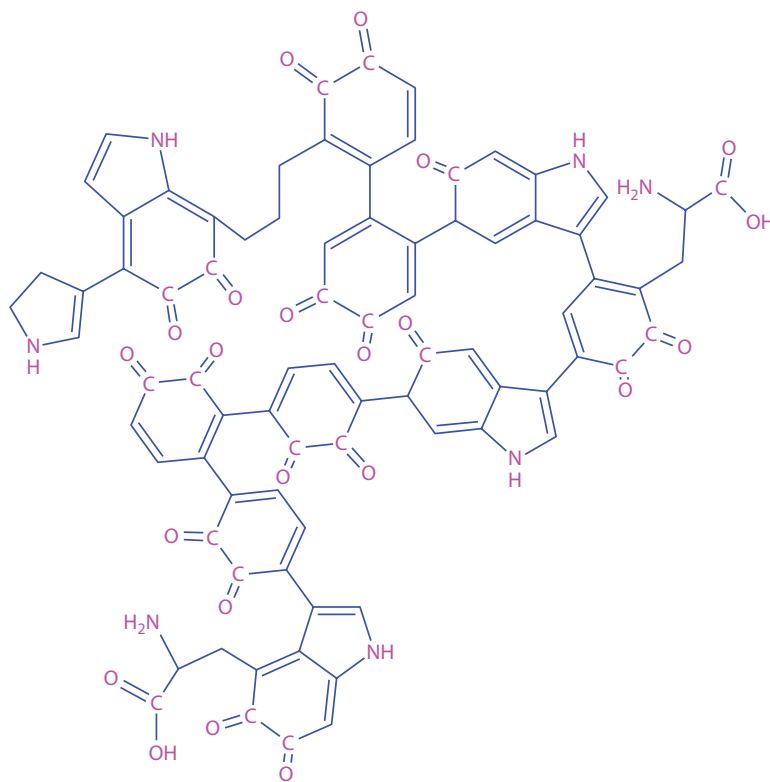


FIGURE 4.16 Representative structure of melanin.

4.12 POLYMER STRUCTURE

Linus Pauling, in 1954, received the Nobel Prize for his insights into the structure of materials, mainly proteins. Pauling showed that only certain conformations are preferred because of intra-molecular and intermolecular hydrogen bonding. While we know much about the structures of natural macromolecules, there is still much to become known.

A most important aspect of secondary structures is supercoiling. *Supercoiling* simply is the coiling of the already helical DNA. The typical DNA structure is the thermally stable form. Two divergent mechanisms are believed responsible for supercoiling. The first, and less prevalent, is illustrated by a telephone cord. The telephone cord is typically coiled and represents the “at rest” or “unstressed” coupled DNA. As I answer the telephone, I have a tendency to twist it in one direction and after answering and hanging up the telephone for awhile, it begins forming additional coils. Thus, additional coiling tends to result in supercoiling. The second, and more common form, involves the presence of less than normal coiling. This can be illustrated by taking a rubber band, breaking one end and then attaching it about a stationary object. Begin braiding the two ends until just prior to a bunching or formation of supercoiling through over coiling. Then separate the two ends pulling them apart. The resulting strain produces supercoiling and illustrates supercoiling resulting in under coiling or under winding. Thus, under winding occurs when there are fewer helical turns than would be expected. Purified DNA is rarely relaxed.

Supercoiling with bacterial DNA gives a largely open, extended, and narrow rather than compacted, multibranched structure. By comparison, the DNA in eukaryotic cells is present in very compacted packages. Supercoiling forms the basis for the basic folding pattern in eukaryotic cells that eventually results in this very compacted structure. Subjection of chromosomes to treatments that partially unfold them shows a structure where the DNA is tightly wound about “beads of proteins” forming a necklace-like arrangement where the protein beads represent precious stones imbedded within the necklace fabric (Figure 4.17). This combination forms the nucleosome, the fundamental unit of organization upon which higher-order packing occurs. The bead of each nucleosome contains eight histone proteins. Histone proteins are small basic proteins with molecular weights between 11,000 and 21,000 and specified by names such as H1 and H2. H1 is especially important and its structure varies to a good degree from species to species, whereas some of the other histones, such as H3 and H4, are very similar. Histones are rich in the amino acid residues from arginine and lysine.

Wrapping of DNA about a nucleosome core compacts the DNA length about sevenfold. The overall compacting though is about 10,000 fold. Additional compacting of about 100-fold is gained from formation of the so-called 30 nm fibers. These fibers contain one H1 within the nucleosome core. This organization does not occur over the entire chromosome but rather is punctuated by areas containing sequence-specific (non-histone containing) DNA-binding proteins. The name



FIGURE 4.17 Illustration of regularly spaced nucleosomes consisting of histone protein bound to supercoiled deoxyribonucleic acid (DNA) with DNA links between the histone bound units forming a 30 nm higher-order fiber.

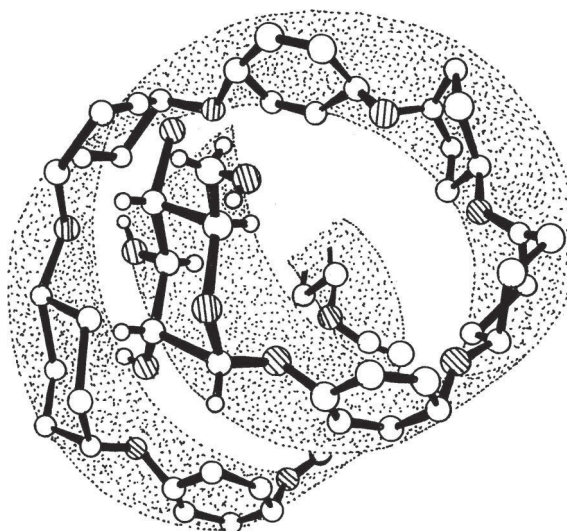


FIGURE 4.18 Helical structural arrangement of amylose derived from α -D-glucose units.

“30 nm fibers” occurs because the overall shape is of a fiber with a 30 nm thickness. The additional modes of compaction are just beginning to be understood but may involve scaffold assisting. Thus, certain DNA regions are separated by loops of DNA with about 20,000–100,000 base pairs with each loop possibly containing sets of related genes.

The scaffold contains several proteins, especially H1 in the core and topoisomerase II. Both appear important to the compaction of the chromosome. In fact, the relationship between topoisomerase II and chromosome folding is so vital that inhibitors of this enzyme can kill rapidly dividing cells, and several drugs used in the treatment of cancer are topoisomerase II inhibitors.

The central theme concerning the major secondary structures found in nature is also illustrated with the two major polysaccharides derived from sucrose, that is, cellulose and a major component of starch, amylose. Glucose exists in one of two forms—an alpha and a beta form where the terms alpha and beta refer to the geometry of the oxygen connecting the glucose ring to the fructose ring.

Cellulose is a largely linear homosaccharide of the beta-D-glucose. Because of the geometry of the beta linkage, individual cellulose chains are generally found to exist as sheets, the individual chains connected through hydrogen bonding. The sheet structure gives cellulose-containing materials good mechanical strength allowing them to act as structural units in plants. Amylose, by comparison, is a linear poly(alpha-D-glucose). Its usual conformation is as a helix with six units per turn (Figure 4.18). Amylose is a major energy source occurring in plants as granules.

4.13 GENETIC ENGINEERING

Genetic engineering is the alteration of an organism’s genetic material. The aim is to introduce into the organism’s genetic material some desirable trait that is otherwise absent. Alternation of genetic material entails the use of polymer chemistry on a molecular (or nano) level making use of somewhat straightforward chemical reactions, many of the reactions employing biological entities, such as enzymes, to carry out these reactions.

Essentially, gene segments are replaced to inject into the altered microorganism genetic material that expresses the desired trait. Today, routine gene alteration is taught in undergraduate laboratories. Even so, specific gene alteration requires extensive planning and is conducted in major research laboratories.

In the broadest sense, genetic engineering refers to any artificial process that alters the genetic composition of an organism. Such alterations can be carried out indirectly through chemical methods, through radiation, or through selective breeding. Today, the term usually refers to the process, whereby genes or portions of chromosomes are chemically altered.

After the alteration of a single, or few, genes, the altered genes reproduce giving much larger numbers of genes with the alteration incorporated in their genome. The term “clone” comes from the Greek word *klon*, meaning a cutting used to propagate a plant. *Cell cloning* is the production of identical cells from a single cell. In like manner, gene cloning is the production of identical genes from a single gene, introduced into a host cell. Today, the term cloning refers to one special type of genetic engineering.

Genes are a chromosomal portion that codes for a single polypeptide or RNA. Gene splicing is currently practiced as the enzymatic attachment of one gene or gene segment to another gene or gene segment. Genes are composed of DNA that can be considered as a specialized polyphosphate polymer. The manipulation of DNA can occur for many reasons. One of these is the production of recombinant DNA. Here we will focus on the production of recombinant DNA. DNA cannot be directly transferred from one organism, the donor, to another recipient organism, the host. Instead, the donor DNA segment is cut and then recombined with a DNA from a host. *E. coli* is typically employed as the host cell since it is itself a harmless bacterium that reproduces rapidly. (But under the wrong conditions, *E. coli* is responsible for many food poisonings.) The *E. coli* then acts as a “factory” that reproduces bacteria that contain the desired modification.

Enzymes, specialized proteins, are used as designing tools for the genetic engineering. One of these enzyme tools consists of *restriction endonucleases* that recognize a specific series of base pairs. They split the DNA at these specific points. This splitting is called “lysing,” which in reality is simply the hydrolysis of DNA units as shown here:



Organisms produce restriction endonucleases that are specific for that organism. Certain restriction endonucleases cut double-stranded DNA asymmetrically in regions called palindromes, that is, regions that “read” (have identical sequences) the same way from left to right on one strand as right to left on the other strand. This produces what is referred to as “sticky ends” that form not only a “cleft” for attachment but also a single-stranded end that has the ability to pair with another complementary single-stranded end. Both strands of the original donor twin strand have a tendency to recombine with complementary strands of DNA from a host that has been treated to produce the complementary strands. The sticky ends, when mixed under the proper conditions in the presence of another enzyme, DNA ligase, combine. The hydrogen bonding between complementary sticky ends reinforces the recombination reaction. The resulting recombination reaction results in a variety of products including the desired recombination of host and donor DNA as well as the combination of the original donor strands and uncombined DNA. The mixture is often treated in one of two manners. The simplest case requires a chemical-resistant gene that is resistant to the employed chemical agent such as tetracycline. The desired recombinant genes survive and are then transferred into the host organism so the new gene can express itself.

In some cases, such as the synthesis of insulin, the recombination mixture is added to a host organism, here *E. coli*. This infected mixture is then plated out and the individual colonies tested for insulin production. Those colonies that produce insulin are further plated out and grown for mass insulin production. Cells that accept the recombinant DNA are called “transformed.” More specialized sequences have been developed to increase the probability of gene incorporation and its successful reproduction.

A second tool employed by the genetic engineer is the enzyme terminal transferase that adds deoxyribonuclease residues to the 3' end of DNA strands creating 3' tails of a single type of residue.

Special modified *plasmid* DNAs, called “vectors” or carriers, are used as host or targets for gene modification. These circularly shaped vectors reproduce autonomously in a host cell. Plasmids have two other important properties. First, they can pass from one cell to another allowing a single “modified” bacterial cell to inject neighboring bacterial cells with this “modification.”

Second, gene material from other cells can be easily formed into plasmids, allowing ready construction of modified carriers.

The steps involved in gene splicing, emphasizing the chemical nature of the individual steps, are as follows:

1. Lysing (which is really simply the hydrolysis of DNA units as shown earlier)
2. Construction of staggered, sticky, ends
3. Recombination or ligation, the reverse of lysing, chemically formation of a phosphate ester as in the following connecting the desired segment to the DNA of the host cell



4. Chemical recombination of vector insertion into the host cell; recombining plasmid genes into the host genetic complement
5. Replication of host cell

There are many uses of recombinant DNA. As noted earlier, one technique that produces recombinant DNA is called cloning. In one cloning technique used for the production of the sheep Dolly in 1996, the DNA nucleus from a female's egg is replaced with a nucleus from another sheep. The egg is placed in the uterus of a third animal, known as the surrogate mother. Dolly is nearly genetically identical to the animal from which the nucleus was obtained but not genetically related to the surrogate mother.

Recombinant DNA has been used in a variety of ways. The growth hormone gene of rainbow trout has been transferred into carp eggs resulting in the transgenic carp producing larger fish. The milk production of dairy cows has been increased by cloning and introducing into the cows the cattle growth hormone bovine somatotropin.

Transgenic strawberry and potato plants have been produced that are frost resistant. Cotton, corn, and soybean plants have been produced with increased resistance to herbicides allowing herbicide use without killing the transgenic crop-producing plants. Larger and smaller varieties of other food-producing plants have been produced using recombinant DNA as have plants that produce certain amino acids needed for our nutrition.

Transgenic bacteria have been produced that can metabolize petroleum products including certain synthetic polymers.

Along with the production of insulin, many other medical uses have been achieved for recombinant DNA. This includes the production of *erythropoietin*, a hormone used to stimulate production of red blood cells in anemic people; tissue *plasminogen activator*, an enzyme that dissolves blood clots in heart attack victims; and *antihemophilic human factor VIII*, used to prevent and control bleeding for hemophilia people. These three important genetically engineered proteins were all cloned in hamster cell cultures.

Gene engineering is the basis of gene therapy where genes are removed, replaced, or altered producing new proteins for the treatment of such diseases as muscular dystrophy, some cancers, adenosine deaminase deficiency, cystic fibrosis, and emphysema.

4.14 DNA PROFILING

DNA profiling is also referred to as DNA fingerprinting and DNA typing. It is used in paternity identification, classification of plants, criminal cases, identification of victims, heredity (of living, recently deceased, and anciently deceased), etc. DNA profiling is a tool that allows a comparison of DNA samples. There are two basic types of DNA profiling: the first one uses *PCR enzymes* and the second employs the *restriction fragment length polymorphism (RFLP) enzymes*. The PCR approach utilizes a sort of molecular copying process where a specific region is selected

for investigation. The PCR approach requires only a few nanograms of DNA. The DNA polymerase makes copies of DNA strands in a process that mimics the way DNA replicates naturally within the cell. Segments are selected for special study and the results used to identify the DNA pattern.

With the exception of identical twins, each individual has a DNA profile that is unique. In excess of 95% of the over 3 billion nucleotides in human DNA are the same. But for every 1000 nucleotides, there is one site of variation or polymorphism. These DNA polymorphisms change the length of the DNA fragments produced by certain restriction enzymes. The resulting fragments are called restriction fragment length polymorphisms or RFLPs. Gel electrophoresis is typically employed to separate the sizes and thus create a pattern of RFLPs. The number and size of the fragments are used to create the DNA profile.

Several steps are involved in creating the genetic fingerprint. First, a sample of cells is obtained from a person's blood, bone, semen, hair roots, or saliva. The individual cells from the sample are split open and DNA isolated. The DNA is treated with restriction enzymes that cleave the DNA strands at specific locations creating fragments of varying lengths and composition. The resulting fragments undergo electrophoresis using a gel that allows the separation of the fragmented DNA. Because the gel is fragile, a thin nylon membrane, covered by a towel, is laid over the gel. As moisture is drawn to the towel from the electrophoresis gel, the DNA fragments are transferred to the nylon membrane. This process is called blotting. The DNA bands are visible to the eye but there are too numerous to be useful. Thus, a radioactive solution is washed over the nylon membrane that binds to select fragments, generally to only 6–20 of the DNA clusters. A sheet of photographic film is placed on top of the nylon membrane that records these cluster sites. The film is then developed producing a pattern of thick-and-thin bands. This pattern is the genetic pattern for that particular sample. This process can take a month or more at commercial labs for routine analysis, but when needed, the analysis can be made in only a day or two or less.

There are different restriction enzymes that cut DNA at different sites. The previous sequence can be repeated several times for the same DNA sample. From a study of each restriction enzyme, a probability that another person will have the same profile is assigned. Thus, one restriction enzyme may have the possibility that another person has the same match of 1 in 100 or 1%. A second restriction enzyme may have the probability of 1 in 1000 or 0.1%. A third restriction enzyme may have a probability for a match being 1 in 500 or 0.2%. If there is a match with all three restriction enzymes, the probability would be $0.01 \times 0.001 \times 0.002$ or 0.00000002 or 0.000002% or 1 part in 50,000,000. There is a caution to using the "multiplication rule," in which DNA sequences are not totally random. In fact, DNA sequence agreements generally diverge as one's ancestors are less closely related.

The RFLP method requires a sample about 100 times larger than required for the PCR approach, but with repeated sequences using different restriction enzymes, RFLP is more precise.

It must be noted that factors leading to DNA degradation, such as moisture, chemicals, bacteria, heat, and sunlight, will impact negatively on DNA profiling since the precise sequences and length of the DNA and DNA fragments may be changed. While DNA, in general, is robust and can exist "alive" over thousands of years (such as the germination of seeds found in the pyramids of Egypt), DNA degradation decreases the probability of precise matches. Also, DNA contamination by addition of DNA from another source greatly confuses the final results.

DNA sequencing has found importance in a wide range of areas. It is being used to identify individuals at greater risk for having certain diseases such as breast cancer. It has allowed taxonomists determine evolutionary relationships among plants, animals, and other life forms. Currently, it is a basis for the so-called Eve theory that says all of us are related to a common woman, called Eve after the Biblical Eve. And more recently, it is believed we also originate from a single male named after the Biblical Adam and that both lived in the same area and time. It is also being used to trace the (ancient) movement of people about Earth. It is used for the screening of certain diseases such as the presence of the sickle-cell gene.

DNA profiling was used to determine whether bones unearthed that were said to be from Jesse James were in fact his. DNA samples were taken from grandchildren and compared to those obtained from the bone material and shown to be similar, so that while it cannot be absolutely said the bones were from Jesse James, DNA evidence was consistent with them being his bones.

4.15 ASPHALT

Nearly 100 billion pounds of asphalt are used annually in the United States. It is the viscous material that is not easily distilled as are more volatile fractions such as gasoline and kerosene are removed from crude oil. They are also found in natural deposits such as the La Brea Tar Pits in California. It is sometimes referred to as bitumen, covered in Section 10.14. Here we will cover additional material related to asphalt.

About 80% of asphalt is employed along with rocks to form our roadways (Picture 4.21). The asphalt acts as the binder for the rock aggregates similar to concrete. Asphalt concrete is the most widely used recycled material, on a weight and percentage basis, in the United States. Over 80% of asphalt from road surfaces removed from resurfacing projects is reused as a component of new construction. Roofing shingles are also a major use of asphalt.

Asphalt is a viscoelastic material and this viscoelasticity must be present over the temperature range where the material is being used. Unfortunately, the asphalt often softens during the summer days allowing rutting or permanent deformation to occur. During the winter, the asphalt chains tend to become more organized resulting in a more brittle material that can undergo thermal and fatigue cracking. With time, the more volatile, shorter chains leave the mixture causing the material to lose some of its flexibility. This process is called aging.

Asphalt emulsions are made by mixing the asphalt generally with petroleum solvents, but some formulations include the more environmentally acceptable water. These emulsions are often employed to resurface concrete and asphalt surfaces such as driveways.

Along with short-chained polymers with up to 150 carbons, asphalt contains a variety of other elements. The composition varies as to the source and treatment of the crude oils. Crude oil from Venezuela contains a particularly high amount of metals, such as iron, nickel, and vanadium, in comparison to crude oil from the Middle East. Some of the asphalts contain polar functional groups such as alcohols, amines, thiols, and carboxylic-containing units. This allows the asphalt chains to aggregate similar to many detergents with the aliphatic units reaching outward from a polar core. For rocks with a mildly polar surface, this results in some binding between the rock surfaces and the asphalt resulting in a more secure material.



PICTURE 4.21 Asphalt material for streets, driveways, highways, and parking spaces.

SUMMARY

1. Physically there is little difference in the behavior, study, or natural and synthetic polymers. The fundamental principles that underpin the behavior of macromolecules apply equally to both synthetic and natural polymers. Both groupings contain members that exhibit characteristics that are unique to that grouping. Even so, differences within even these groupings are by degree rather than kind with the fundamental laws continuing to be applicable.
2. Contributions from studying both natural and synthetic polymers are being used to forward the science of both sets of macromolecules.
3. Organic polymers are responsible for the very life—both plant and animal—that exists. Their complexity allows for the variety that is necessary for life to occur, to reproduce, and to adapt. Structures of largely linear natural and synthetic polymers can be divided into primary structures used to describe the particular sequence of (approximate) repeat units; secondary structure used to describe the molecular shape or conformation of the polymer; tertiary structure that describes the shaping or folding of macromolecules; and quaternary structure that gives the overall shape of groups of tertiary-structured macromolecules. The two basic secondary structures are helices and sheets.
4. Polysaccharides are the most abundant, on a weight basis, naturally occurring organic polymer. They are truly complex molecules with most structures representable on only an “average” basis. They are diverse with respect to both occurrence and size. The most important, on a knowledge, weight, and use basis, are cellulose and starch. Cellulose is composed largely of D-glucose units that are associated with other materials such as lignin. Cotton is one of the purest forms of cellulose though we get most of our cellulose from wood pulp. Cellulose becomes soluble in aqueous solutions only when the hydrogen bonding within the cellulose is broken.
5. While cellulose is used extensively itself in the form of paper and paper-based products, it also forms the basis of a number of synthetic materials including a variety of acetylated products such as rayon.
6. Starch is composed of two major components—amylopectin and amylose. It is the second most abundant polysaccharide and found largely within plants.
7. Proteins are composed of 20 different alpha-amino acids and contain peptide linkages similar to those present in polyamides. With the exception of glycine, all the amino acids contain a chiral carbon. The geometrical shape and behavior of the giant proteins are a product of the various preferred geometries that allow the molecules to balance factors such as preferred bond angle, secondary bonding forces emphasizing hydrogen bonding, size, shape, hydrophobic/hydrophilic interactions, external/internal chemical environments, and cross-linking. Small chains of amino acids are referred to as peptides.
8. Secondary structures for proteins are generally fibrous and globular. Proteins such as keratin, collagen, and elastin are largely fibrous and have secondary structures of sheets and helices. Many of the globular proteins are composed of protein chains present in secondary structures approximating helices and sheets.
9. Enzymes are one important group of proteins. They serve as natural catalysts immobilizing various components that will be later joined or degraded.
10. The two major types of nucleic acids are DNA and RNA. Nucleic acids are polyphosphate esters containing the phosphate, sugar, and base moieties. Nucleic acids contain one of five purine/pyrimidine bases that are coupled within double-stranded helices. DNA, which is an essential part of the chromosome of the cell, contains the information for the synthesis of protein molecules. For double-stranded nucleic acids, as the two strands separate, they act as a template for the construction of a complementary chain. The reproduction or duplication of the DNA chains is called replication. The DNA undergoes semiconservative replication where each of the two new strands contains one of the original strands.
11. The flow of biological genome knowledge is from DNA to RNA via transcription and from RNA to direct protein synthesis via translation.

12. Polyisoprenes form the basis of many natural polymers including the two most widely known natural plastics gutta-percha and balata and an elastomer known as *Hevea brasiliensis* or NR. The hard plastics balata and gutta-percha are trans isomers while NR is the cis isomer of 1,4-polyisoprene. The polymer chain of amorphous NR and other elastomers uncoils during stretching and returns to its original low-entropy form when the material is above its T_g . Chain slippage is minimized through the presence of cross-links. Unlike other solids, stretched rubber contracts when heated. The long-range elasticity is dependent on the absence of strong intermolecular forces. Eventually, NR formed the basis of the rubber industry through gaining knowledge of such factors as cross-linking that allowed the material to remain coherent but elastomeric even when exposed to moderate temperatures.
13. Genetic engineering is based on chemical manipulations that are exactly analogous to those carried out by chemist in basic chemistry laboratories, but it involves the use of biological agents.
14. Melanins are polymeric agents that play many roles in nature including forming our skin pigmentation and with its growth through exposure to sunlight, acting to protect us from the harmful effects of the sunlight.

GLOSSARY

Accelerator: Catalyst for the vulcanization of rubber.

Alkali cellulose: Cellulose that have been treated with a strong basic solution.

α -Cellulose: Cellulose that is not soluble in 17.5% basic solution.

α Helix: Right-handed helical conformation.

Amylopectin: Highly branched starch polymer with branches or chain extensions on carbon 6 of the anhydroglucose repeating unit.

Amylose: Linear starch polymer.

Antioxidant: Compound that retards polymer degradation.

Balata: Naturally occurring *trans*-1,4-polyisoprene.

β Arrangement: Pleated sheetlike conformation.

β -Cellulose: Cellulose soluble in 17.5% basic solution but not soluble in 8% caustic solution.

Boeseken–Haworth projections: Planar hexagonal rings used for simplicity instead of staggered chain forms.

Carbohydrate: Organic compound often with an empirical formula CH_2O ; sugars, starch, and cellulose are carbohydrates.

Carbon black: Finely divided carbon used for the reinforcement of rubber.

Carboxymethylhydroxyethylcellulose (CMHEC): Made from the reaction of sodium chloroacetate and hydroxyethylcellulose.

Carrageenan: Mixture of several polysaccharides containing D-galactose units; obtained from seaweed.

Casein: Milk protein.

Cellobiose: Repeat unit in cellulose.

Cellophane: Sheet of cellulose regenerated by the acidification of an alkaline solution of cellulose xanthate.

Celluloid: Product from a mixture of cellulose nitrate and camphor.

Cellulose: Linear polysaccharide consisting of many anhydroglucose units joined by beta-acetal linkages.

Cellulose acetate: Product from the acetylation of cellulose.

Cellulose nitrate: Made from the reaction of cellulose and concentrated nitric acid; also known as gun cotton.

Cellulose xanthate: Product of soda cellulose and carbon disulfide.

Chitin: Polymer of acetylated glucosamine present in the exoskeletons of shellfish.

Collagen: Protein present in connective tissue.

Compounding: Processing of adding essential ingredients to a polymer such as rubber.

C-terminal amino acid: Amino acid with a carboxylic acid end group.

Cyclodextrins: Oligomeric cyclic products formed from the reaction of starch treated with a certain enzyme.

Degree of substitution (DS): Number that designates the average number of reacted hydroxyl groups in each anhydroglucose unit in cellulose or starch.

Denaturation: Change in conformation of a protein resulting from heat or chemicals.

Deoxyribonucleic acid (DNA): Nucleic acid in which deoxyribose unit is present; composes the human genome.

Dextran: Branched polysaccharide synthesized from sucrose by bacteria.

DNA profiling: Identification method based on variations between individual's DNA.

Drying: Jargon used to describe the cross-linking of unsaturated polymers in the presence of air and a heavy metal catalyst (drier).

Elastin: Protein that is the major material of arterial blood vessels and ligaments that is noted for its flexibility.

Enzyme: Protein with specific catalytic activity.

Ester gum: Ester of rosin and glycerol.

Ethylhydroxyethylcellulose (EHEC): Nonionic mixed ether formed from HEC and ethyl chloride.

Fibrillar protein: Hairlike, insoluble, intermolecularly hydrogen-bonded protein.

Fibrils: Threadlike strands or bundles of fibers.

Fossil resins: Resins obtained from the exudate of prehistoric trees.

Galalith: Commercial casein plastics.

γ -Cellulose: Cellulose soluble in 8% caustic solution.

Genome: Total genetic information contained in a cell, organism, or virus.

Globular proteins: Proteins with an overall globular structure formed from contributions of secondary structures including sheets and helices.

Glycine: Simplest and only nonchiral alpha-amino acid.

Glycogen: Highly branched polysaccharide that serves as the reserve carbohydrate in animals.

Guayule: Shrub that produces *cis*-1,4-polyisoprene rubber.

Gutta percha: Naturally occurring *trans*-1,4-polyisoprene.

***Hevea brasiliensis*:** Natural rubber, NR.

Humic acid: Polymeric aromatic carboxylic acid found in lignite.

Hydrocellulose: Cellulose degraded by hydrolysis.

Hydroxyethylcellulose (HEC): Produced from alkaline cellulose and ethylene oxide.

Hydroxypropylcellulose: Thermoplastic cellulose ether formed from alkaline cellulose and propylene oxide.

Isoelectric point: pH at which an amino acid does not migrate to either the positive or negative pole in a cell.

Keratin: Fibrillar protein.

Latex: Stable dispersion of polymer particles in water.

Lignin: Noncellulosic resinous component of wood.

Mercerized cotton: Cotton fiber that has been immersed in caustic solution, usually under tension, and washed with water removing the excess caustic.

Methylcellulose (MC): Formed from alkaline cellulose and chloromethane.

Myosin: Protein present in muscle.

Native cellulose: Naturally occurring cellulose; like cotton.

N-terminal amino acid: Amino acid with an amino end group.

Nucleoside: Contains a pentose and base.

Nucleotide: Contains a phosphate, pentose, and base.

Oligosaccharide: Low-molecular-weight polysaccharide.

Polynucleotide: Nucleic acid.

Polypeptide: Protein; often used for low-molecular-weight proteins.

Polysaccharide: Polymer containing many sugar units; like cellulose and starch.

Primary structure: Term used to describe the primary configuration present in a protein chain.

Prosthetic group: Nonproteinaceous group conjugated (connected) to a protein.

Protein: Polyamide in which the building blocks are alpha-amino acids joined by peptide (amide) linkages.

- Purine base:** Compounds consisting of two fused heterocyclic rings, namely, a pyrimidine and an imidazole ring; essential part of nucleic acids.
- Pyrimidine:** A 1,3-diazine; essential part of nucleic acids.
- Racked rubber:** Stretched rubber cooled below its T_g .
- Rayon:** Cellulose regenerated by acidification of a cellulose xanthate (viscose) solution.
- Recent resins:** Resins obtained from exudates of living trees.
- Regenerated cellulose:** Cellulose obtained by precipitation from solution.
- Replication:** Term used to describe duplication such as the duplication of DNA.
- Retrogradation:** Process whereby irreversible gel is produced by the aging of aqueous solutions of amylose starch.
- Ribonucleic acid (RNA):** Nucleic acid in which ribose units are present. Essential units of life and replication.
- Schweitzer's solution:** Ammoniacal solution of copper (II) hydroxide.
- Secondary structure:** Term used to describe the conformation of a protein molecule such as a helix.
- Shellac:** Natural polymer obtained from the excreta of insects in Southeast Asia.
- Starch:** Linear or branched polysaccharides of many anhydroglucose units joined by an alpha linkage; amylose is the linear fraction and amylopectin is the branched fraction.
- Tenacity:** Term used for the tensile strength of a polymer.
- Terpene:** Class of hydrocarbons having the empirical formula C_5H_8 .
- Tertiary structure:** Term used to describe the shape or folding of a protein.
- Transcription:** Term used to describe the transfer of information from DNA to RNA.
- Translation:** Term used to describe the transfer of information from RNA to protein synthesis.
- Viscose:** Alkaline solution of cellulose xanthate.
- Zwitterion:** Dipolar ion of an amino acid.

EXERCISES

1. Why is starch digestible by humans? Why is cellulose not digestible by humans?
2. How does cellobiose differ from maltose?
3. Why is cellulose stronger than amylose?
4. How does the monosaccharide hydrolytic product of cellulose differ from the hydrolytic product of starch?
5. What is paper made from?
6. How many hydroxyl groups are present on each anhydroglucose unit in cellulose?
7. Which would be more polar: tertiary or secondary cellulose acetate?
8. Why would you expect chitin to be soluble in hydrochloric acid?
9. Which is more apt to form a helix: (a) amylose or (b) amylopectin?
10. Why is amylopectin soluble in water?
11. Define a protein in polymer science language.
12. Which α -amino acid does not belong to the L-series of amino acids?
13. To which pole will an amino acid migrate at a pH above its isoelectric point?
14. Why is collagen stronger than albumin?
15. What are the requirements for a strong fiber?
16. Which protein would be more apt to be present in a helical conformation: (a) a linear polyamide with small pendant groups or (b) a linear polyamide with bulky pendant groups?
17. What is the difference between the molecular weight of (a) ribose and (b) deoxyribose?
18. What is the repeating unit in the polymer DNA?
19. Which is more acidic: (a) a nucleoside or (b) a nucleotide?
20. What base found in DNA is not present in RNA?
21. Why would you predict helical conformations for RNA and DNA?
22. If the sequence of one chain of a double helix of DNA is ATTACGTCAT, what is the sequence of the adjacent chain?
23. Why is it essential to have trinucleotides rather than dinucleotides as condoms for directing protein synthesis?

24. How do the configurations differ for (a) gutta-percha and (b) natural rubber?
25. What polymer formation is responsible for tanning?
26. Will the tensile force required to stretch rubber increase or decrease as the temperature is increased?
27. Does a stretched rubber band expand or contract when heated?
28. List three requirements for an elastomer.
29. Why is there an interest in the cultivation of guayule?
30. Are the polymerization processes for synthesis and natural *cis*-polyisoprene (a) similar or (b) different?
31. What does the presence of C_5H_8 units in NR indicate?
32. Why is *E. coli* most often used in gene splicing?
33. Why does a rubber band become opaque when stretched?
34. What is the most important contribution to retractile forces in highly elongated rubber?
35. What is present in the so-called vulcanized rubber compounds?
36. When a rubber band is stretched, what happens to its temperature?
37. Why are natural plastics not used anymore?
38. What type of solvent would you choose for shellac?
39. Why is lignin sometimes referred to as being a two-dimensional polymer?
40. Which is a polymer: (a) rosin or (b) ester gum?
41. If the annual production of paper is over 100 million tons, how much lignin is discarded from paper production annually?
42. Might an article molded from Galalith be valuable?

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Step-Reaction Polymerization (Polycondensation Reactions)

In Chapter 2, we noted that there is a direct relationship between polymer structure and their physical properties. In this chapter, we examine condensation polymers that primarily have relatively strong attractions, secondary bonding, between and within polymer chains. Because of these strong secondary bonding attractions, these polymers are typically strong requiring relatively a lot of force to elongate them. Many of them are synthesized so that there is good symmetry allowing the chains to more closely pack together, further enhancing the magnitude of the secondary bonding and increasing the glass transition of the materials. When these materials are allowed to form mainly crystals, they can act as fibers, and when they are processed so that the noncrystalline fraction is large, they can act as plastics.

Since most condensation polymers are formed from stepwise kinetics, we will also focus on this kinetic process in this chapter. Even so, some of these polymers can be synthesized employing ring-opening polymerizations (ROPs) that employ the chain polymerization process for synthesis rather than the stepwise process for formation. The bulk of discussion for chain polymerization kinetics is contained in the following several chapters rather than here. We will begin with a comparison between the two major polymer types and kinetics of polymerization.

5.1 COMPARISON BETWEEN POLYMER TYPE AND KINETICS OF POLYMERIZATION

There is a large, but not total, overlap between the terms condensation polymers and stepwise kinetics and the terms addition (or vinyl) polymers and chain kinetics. In this section, we will look at each of these four terms and illustrate the similarities and differences between them.

The terms “**addition**” and “**condensation**” polymers were first proposed by Carothers and are based on whether the repeat unit of the polymer contains the same atoms as the monomer. An addition polymer has the same atoms as the monomer in its repeat unit. Since many of the important addition polymers are formed from vinyl reactants, many addition polymers are also referred to as “**vinyl polymers**” (5.1).



where

“X” is CH₃ for polypropylene

H for polyethylene

C₆H₅ for polystyrene, etc.

The atoms in the backbone of addition polymers are almost always only carbon.

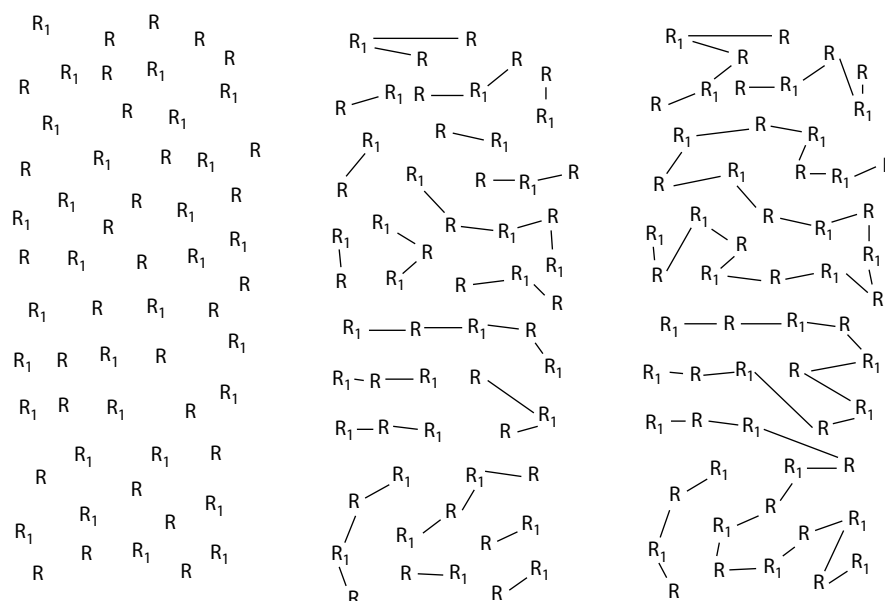
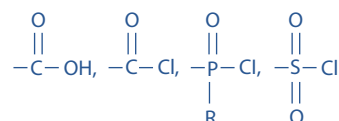


FIGURE 5.1 Depiction of stepwise chain growth for monomers R and R_1 as the polymerization begins (far left) and progressing toward the right.

Condensation polymers generally contain fewer atoms in the polymer backbone than in the reactants because of the formation of by-products during the polymerization process and the backbone contains noncarbon atoms.



where A-X can be most Lewis bases such as $-\text{NH}_2$, $-\text{SH}$, and $-\text{OH}$ and B-Y can be Lewis acids such as



The corresponding polymerizations to form these two polymer types are typically addition and condensation polymerizations.

The term “stepwise kinetics,” or “step-growth kinetics,” refers to polymerizations in which the polymer’s molecular weight increases in a slow, stepwise manner as reaction time increases. Figure 5.1 contains a depiction of the stepwise polymerization process. Initially, there is only

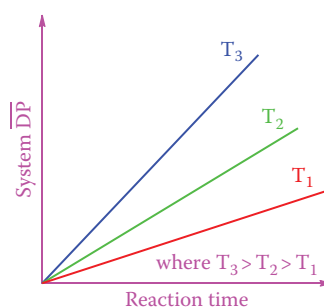
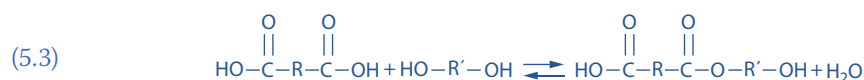


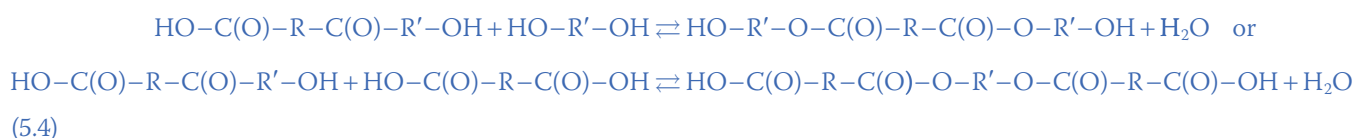
FIGURE 5.2 System molecular weight for stepwise kinetics as a function of reaction time and reaction temperature, T .

monomer R and R_1 present (far left). After some time, all the monomer has reacted, yet no high-molecular-weight chains are found with the greatest DP being 2.5 (middle). As polymerization continues, longer chains grow with a high DP of 10 (far right) for this depiction. Eventually, all of the chains will connect finally giving polymer. Figure 5.2 contains a representative plot of DP as a function of time for this process.

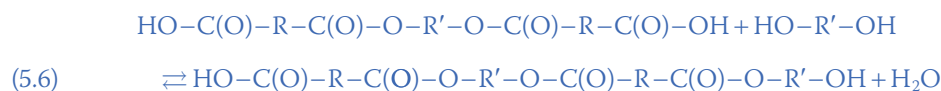
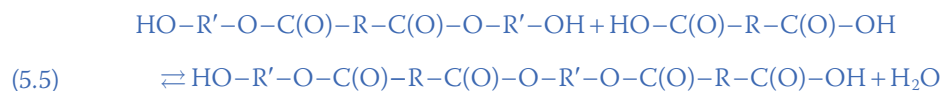
The formation of polyesters from a dialcohol (diol) and a dicarboxylic acid (diacid) will be used to illustrate the stepwise kinetic process. Polymer formation begins with one diol molecule reacting with one diacid forming essentially one repeat unit of the eventual polyester (Equation 5.3).



This ester unit can now react with either an alcohol or acid group producing chains ending with either two active alcohol functional groups or two active acid groups (Equation 5.4):

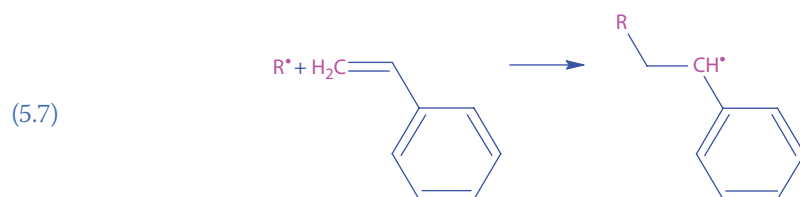


The chain with two alcohol ends can now condense with a molecule containing an acid end (5.5), and the chain with two acid ends can now condense with a molecule containing an alcohol group (5.6) resulting in molecules that contain one acid and one alcohol group at their ends. This reaction continues through the reaction matrix whenever molecules with the correct functionality, necessary energy of activation, and correct geometry collide. The net effect is the formation of dimers, trimers, etc., until polymer is formed.



The reactants are consumed with few long chains formed until the reaction progresses toward total reaction of the chains with themselves. Thus, polymer formation occurs one step at a time, hence the name “stepwise” kinetics.

Chain-growth reactions require initiation to begin chain growth. We will look at the free radical growth forming polystyrene to illustrate chain growth. Here, the initiation of a styrene molecule, R, will illustrate the chain-growth process. The initiator reacts with a styrene monomer creating a free radical active chain end. This free radical chain end then reacts with another styrene monomer that, in turn, reacts with another styrene monomer, etc. until termination stops chain growth with the formation of a polystyrene polymer chain (Figure 5.3). Polystyrene chains are formed from the beginning of the polymerization process with growth occurring through formation of polymer chains. As the first chain is formed (Figure 5.3; middle), only polymer and monomer are present. As additional polymer chains are formed (Figure 5.3; right), the polymer mix still consists of only polymer chains and unreacted monomer. This is shown in the following sequences:



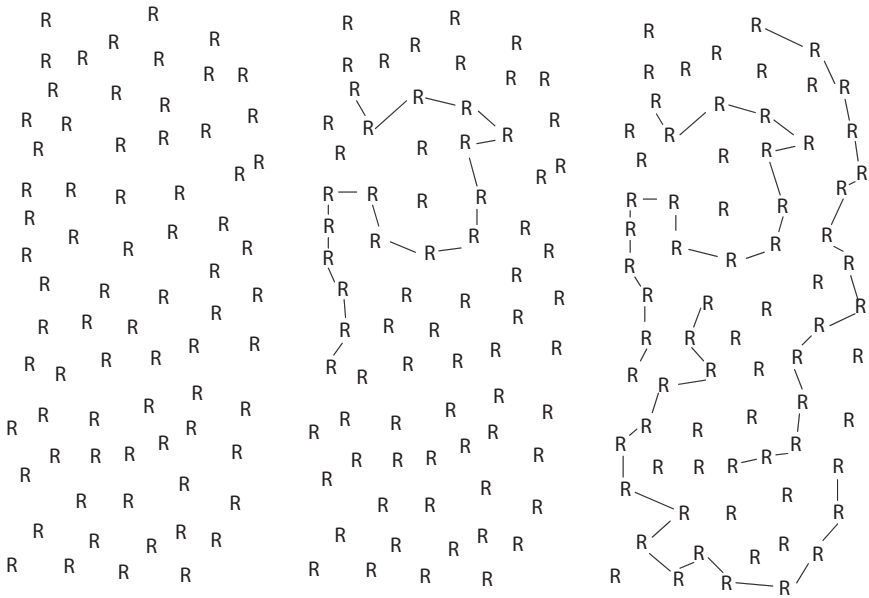
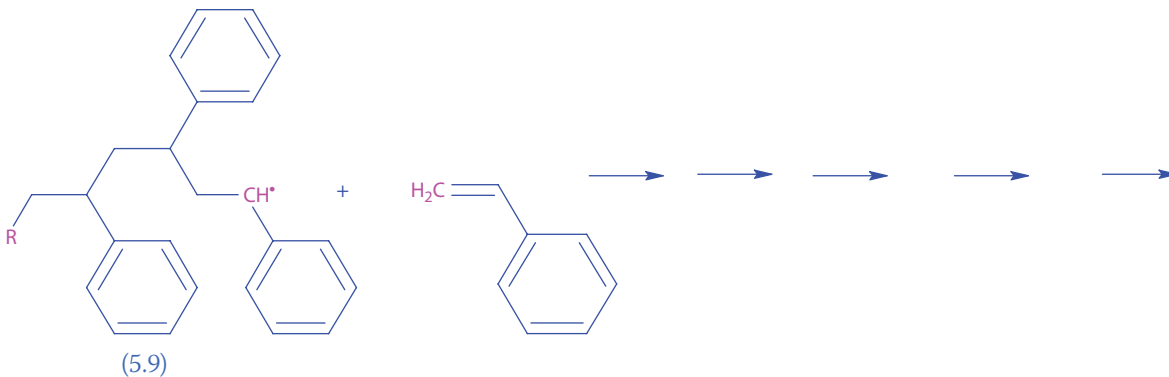
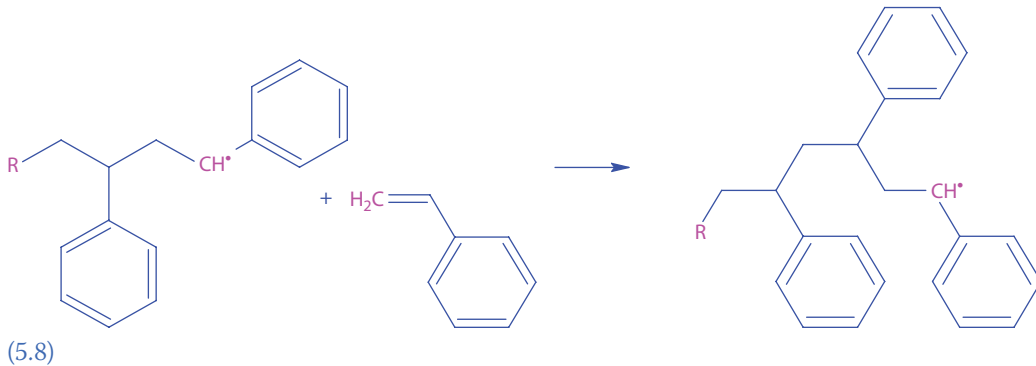


FIGURE 5.3 Molecular weight for chain-growth kinetics as a function of reaction time beginning with only monomer (R; far left) with reaction progressing toward the right.



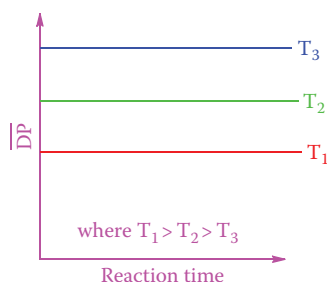


FIGURE 5.4 Idealized average molecular weight of formed polymer as a function of reaction time and temperature, T , for chain-type polymerization.

The average DP for the entire system, neglecting unreacted monomer, does not markedly change as additional polymer is formed (Figure 5.4). Also, unlike the stepwise process, average chain length decreases with an increase in reaction temperature. There is more about this in Chapters 6 and 7.

Both the stepwise and chain-wise polymerizations produce polymers that are polydisperse with respect to chain lengths.

Most addition polymers are formed from polymerizations exhibiting chain-growth kinetics. This includes the typical polymerizations, via free radical or some ionic mode, of the vast majority of vinyl monomers such as vinyl chloride, ethylene, styrene, propylene, methyl methacrylate, and vinyl acetate. By comparison, most condensation polymers are formed from systems exhibiting stepwise kinetics. Industrially, this includes the formation of polyesters and polyamides (nylons). Thus, there exists a large overlap between the terms stepwise kinetics and condensation polymers and chain-wise kinetics and addition (or vinyl) polymers. A comparison of the two types of systems is given in Table 5.1.

Even so, there is not a total overlap between the various characteristics of vinyl-chain kinetics and condensation-step kinetics. The following are examples illustrating the lack of adherence to this overlap:

1. The formation of polyurethanes (PUs) and polyureas typically occurs through stepwise kinetics with the polymer backbones clearly containing noncarbon atoms. Yet no by-product is released through the condensation process because condensation occurs through an internal rearrangement and shift of the hydrogen—neither steps resulting in expulsion of a by-product.

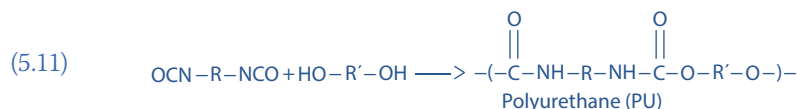
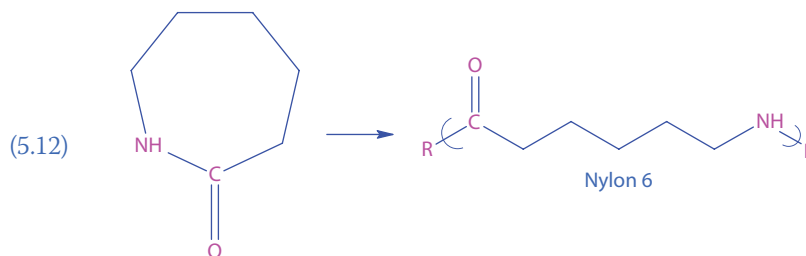


TABLE 5.1 Comparison between Stepwise and Chain-Wise Polymerizations

Chain	Step
Growth occurs by addition of one unit at a time.	Any two unlike molecular units can react.
Monomer concentrations decrease steadily throughout the polymerization.	Monomer disappears early in the reaction.
Polymer chains are formed from the beginning of the polymerization and throughout the process.	Polymer chain length increases steadily during the polymerization.
Average chain length for reacted species remains approximately constant throughout the polymerization.	Average molecular weight for the reaction (for the reacted species) increases throughout the polymerization.
As reaction time is increased, polymer yield increases, but molecular weight remains about the same.	High “extents” of reaction are required to obtain high chain lengths.
Reaction mixture contains almost only unreacted monomer, polymer, and very little growing polymer chains.	Reaction system contains various stages, chain lengths, of product present in a calculable distribution.

2. Internal esters (lactones) and internal amides (lactams) are readily polymerized through a chain-wise kinetic process forming polyesters and polyamides, clearly condensation polymers with respect to having noncarbons in the backbone but without expulsion of a by-product.



A similar ROP with ethylene oxide forming poly(ethylene oxide) forms a noncarbon backbone via a chain-wise kinetic process.



These polymerizations are referred to as ROPs.

3. Interfacially formed condensation polymers such as polyesters, polycarbonates, nylons, and PUs are typically formed on a microscopic level in a chain-growth manner due to comonomer migration limits and largely because of the highly reactive nature of the reactants employed for such interfacial polycondensations.

5.2 INTRODUCTION

While condensation polymers account for only a modest fraction of all-synthetic polymers, most natural polymers are of the condensation type. The first all-synthetic polymer, Bakelite, was produced by the stepwise polycondensation of phenol and formaldehyde.

As shown by Carothers in the 1930s, the chemistry of condensation polymerizations is essentially the same as classic condensation reactions leading to the formation of monomeric esters, amides, and so on. The principal difference is that the reactions used for polymer formation are bifunctional instead of monofunctional.

Table 5.2 contains a list of industrially important synthetic condensation polymers.

5.3 STEPWISE KINETICS

The kinetics for stepwise polycondensation reactions and the kinetics for monofunctional aminations and esterifications, for example, are similar. Experimentally, both kinetic approaches are essentially identical. Usual activation energies (120–240 kJ/mol) require only about one collision in 10^{12} – 10^{15} to be effective in producing polymer at 100°C, whereas for the vinyl reactions, the activation energies are much smaller (8–20 kJ/mol), with most collisions of proper orientation being effective in lengthening the chain. This is in agreement with the slowness of the stepwise process in comparison to chain polymerizations.

While more complicated situations can occur, we will consider only the kinetics of simple polyesterification. The kinetics of most other common polycondensations follows an analogous pathway.

For uncatalyzed reactions where the diacid and diol are present in equimolar amounts, one diacid is experimentally found to act as a catalyst. The experimental expression dependencies are described as follows:

$$(5.14) \quad \text{Rate of polycondensation} = -\frac{d[A]}{dt} = k[A]^2[D]$$

where

[A] is the concentration of diacid

[D] is the diol concentration

TABLE 5.2 Properties and Uses of Some Important Synthetic Condensation-Type Polymers

Type (Common Name)	Typical Properties	Typical Uses
Polyamides (nylons)	Good balance of properties; high strength, good elasticity and abrasion resistance, and good toughness; favorable solvent resistance, outdoor weathering, moisture resistance	Fibers, about ½ of all nylon fiber goes into tire cord; rope, cord, belting, fiber cloths, thread, hose, undergarments, dresses; and plastics, used as an engineering material, substitute for metal bearings, bearings, cams, gears, rollers, jackets on electrical wire
Polyurethanes	Elastomers, good abrasion resistance, hardness, resistance to grease, elasticity; fibers, high elasticity, excellent rebound; coatings, good resistance to solvents and abrasion, good flexibility, impact resistance; foams, good strength per weight, good rebound, high-impact strength	Four major forms are used: fibers (swimsuits, foundation garments), elastomers (industrial wheels, heel lifts), coatings (floors where impact and abrasion resistance are required, bowling pins), foams (pillows, cushions)
Polyureas	High T_g , fair resistance to greases, oils, solvents	Not widely used
Polyesters	High T_g and T_m ; good mechanical properties, resistance to solvents and chemicals; good rebound low moisture absorption, high modulus; film, high tensile strength (about that of steel), stiff, high resistance to failure on repeated flexing, high-impact strength, fair tear strength	Fibers, garments, permanent press and “wash and wear” garments, felts, tire cord, film (magnetic recording tape, high grade film)
Polyethers	Good thermoplastic behavior, water solubility; moderate strength and stiffness	Sizing for cotton and synthetic fibers; stabilizers for adhesives, binders, and film-formers in pharmaceuticals; thickeners; production of films
Polycarbonates	Crystalline with good mechanical properties, high-impact strength; good thermal and oxidative stability, transparent, self-extinguishing, low moisture absorption	Machinery and business parts; DVD and CDs
Phenol-formaldehyde resins	Good heat resistance, dimensional stability, resistance to cold flow, solvent, dielectric properties	Used in molding applications; appliances, TVs, automotive parts, filler, impregnating paper, varnishes, decorative laminates, electrical parts, countertops, toilet seats; adhesive for plywood, sandpaper, brake linings, abrasive wheels
Polyanhydrides	Intermediate physical properties; medium to poor T_g and T_m	No large industrial applications
Polysulfides	Outstanding oil and solvent resistance; good gas impermeability, resistance to aging, ozone, bad odors, low tensile strength, poor heat resistance	Gasoline hoses, tanks, gaskets, diaphragms
Polysiloxanes	Available in a wide range of physical states, from liquids to greases, to waxes, to resins, to elastomers; excellent high and moderate low temperature physical properties; resistant to weathering and lubricating oils	Fluids, cooling and dielectric fluids, in waxes and polishes; as antifoam and mold release, for paper and textile treatment elastomers, gaskets, seals, cable, wire insulation, hot liquids and gas movement, surgical and prosthetic devices, sealing compounds; resins, varnishes, paints, encapsulating and impregnating agents
Polyphosphate and poly-phosphonate esters	Good fire resistance, fair adhesion, moderate moisture stability, fair temperature stability	Additives promoting flame retardance; adhesive for glass (since it has a similar refractive index), pharmaceuticals, surfactant

Since $[A] = [D]$, we can write

$$(5.15) \quad -\frac{d[A]}{dt} = k[A]^3$$

Rearrangement gives

$$(5.16) \quad -\frac{d[A]}{A^3} = k dt$$

Integration of Equation 5.16 over the limits of $A = A_0$ to $A = A_t$ and $t = 0$ to $t = t$ gives

$$(5.17) \quad 2kt = -\frac{1}{[A_0]^2} - \frac{1}{[A_0]^2} = \frac{1}{[A_t]^2} + \text{Constant}$$

It is usual to express Equation 5.17 in terms of the extent of reaction, p , where p is defined as the fraction of functional groups that have reacted at time t . Thus, $1 - p$ is the fraction of groups unreacted. A_t is in turn $A_0 \times (1 - p)$, that is,

$$(5.18) \quad A_t = A_0(1 - p)$$

Substitution of the expression for A_t from Equation 5.18 into Equation 5.17 and rearrangement gives

$$(5.19) \quad 2A_0^2kt = \frac{1}{(1-p)^2} + \text{Constant}$$

which is the equation of a straight line, that is,

$$mx = y + b$$

where

$$m = 2A_0^2k$$

$$x = t$$

$$y = 1/(1 - p)^2$$

$$b \text{ is constant}$$

A plot of $1/(1 - p)^2$ as a function of time should be linear with a slope $2A_0^2k$ from which k is determined. Determination of k at different temperatures allows the calculation of activation energy. Thus, one definition of the specific rate constant is $k = Ae^{-E_a/Rt}$. The log of both sides gives $\log k = \log A - E_a/Rt$, which again is the equation of a straight line where $y = \log k$, $b = \log A$, $m = -E_a/R$, and $x = 1/t$ where E_a is the activation energy, A is constant, k is the specific rate constant, and t is the temperature.

The number-average degree of polymerization can be expressed as

$$(5.20) \quad \overline{DP}_n = \frac{\text{Number of original molecules}}{\text{Number of molecules at time } t} = \frac{N_0}{N} = \frac{A_0}{A_t}$$

Thus,

$$(5.21) \quad \overline{DP}_n = \frac{A_0}{A_t} = \frac{A_0}{A_0(1 - p)} = \frac{1}{1 - p}$$

The relationship given in Equation 5.21, $\overline{DP}_n = 1/(1 - p)$, is called the “Carothers’ equation” because it was first found by Carothers while working with the synthesis of polyamides (nylons). It is arguably the most important mathematical relationship in synthetic polymer science. For many years after Carothers and his team found this relationship, many in the polymer field were unaware of it and so “wasted” much effort and material that could have been avoided had they employed this relationship.

For an essentially quantitative synthesis of polyamides where p is 0.9999, the \overline{DP}_n is approximately 10,000, the value calculated using Equation 5.21.

$$(5.22) \quad \overline{DP}_n = \frac{1}{1-p} = \frac{1}{1-0.0000} = \frac{1}{0.0001} = 10,000$$

Thus, the Carothers' equation allows a determination of maximum \overline{DP} as a function of extent of polymerization and the purity of reactants. This value of 10,000 Da is sufficient to produce polyesters that will give strong fibers. The high value of p is decreased, as is the \overline{DP} , if impurities are present or if some competing reaction, such as cyclization, occurred. Since the values of k at any temperature can be determined from the slope ($2kA_0^2$) when $1/(1-p)^2$ is plotted against t , \overline{DP}_n at any time t can be determined from the expression

$$(5.23) \quad (\overline{DP}_n)^2 = 2kt[A_0]^2 + \text{Constant}$$

Much longer times are required to effect formation of high polymer polyesters in uncatalyzed esterifications than for acid or base-catalyzed systems. For catalyzed systems, since the added acid or base is a catalyst, its apparent concentration does not change with time; thus, it is not included in the kinetic rate expression. In such cases, the reaction follows the rate expression

$$(5.24) \quad \text{Rate of polycondensation} = -\frac{d[A]}{dt} = k[A][B]$$

For $[A] = [B]$, we have

$$(5.25) \quad -\frac{d[A]}{dt} = k[A]^2$$

and rearrangement gives

$$(5.26) \quad -\frac{d[A]}{[A]^2} = kt$$

which on integration and subsequent substitution gives

$$(5.27) \quad kt = \frac{1}{A_t} - \frac{1}{A_0} = \frac{1}{A_0(1-p)} - \frac{1}{A_0}$$

Rearrangement gives

$$(5.28) \quad A_0kt = \frac{1}{(1-p)} - 1 = \overline{DP}_n - 1$$

which predicts a linear relationship of $1/1-p$ with reaction time. This is shown in Figure 5.5.

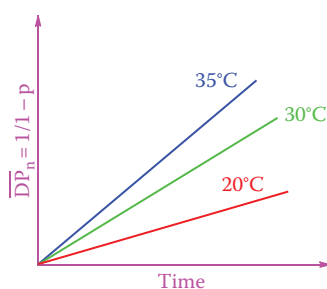


FIGURE 5.5 Plot of chain length, \overline{DP}_n , as a function of reaction time for the acid-catalyzed condensation of ethylene glycol with terephthalic acid producing poly(ethylene terephthalate).

Useful polymers are not obtained unless the value for the fractional conversion p is at least 0.990, that is, a \overline{DP} greater than 100.

We can also calculate the weight average chain length as follows. We have that

$$(5.29) \quad \overline{DP}_w = \frac{1+p}{1-p}$$

The molecular weight distribution is defined as M_w/M_n or $\overline{DP}_w/\overline{DP}_n$ and

$$(5.30) \quad \frac{\overline{DP}_w}{\overline{DP}_n} = \frac{1+p}{1-p} \text{ divided by } \frac{1}{1-p} = 1+p$$

where p is near or equal to 1, that is, for a high-molecular-weight situation,

$$(5.31) \quad \frac{\overline{DP}_w}{\overline{DP}_n} = 1+1 = 2$$

for condensation polymerizations.

Of note, the molecular weight distribution for condensation polymers formed from stepwise kinetics is generally small in comparison to vinyl polymers formed from the chain-wise kinetics where $\overline{DP}_w/\overline{DP}_n$ values of 4–20 are not unusual.

It is important to note that the rate constant k for reactions for similar monofunctional compounds is essentially the same as for the difunctional compounds used in the formation of polycondensation polymers. Likewise, as in the case of reactions of small molecules, the rate constant k increases with temperature in accordance with the Arrhenius equation (Equation 5.32):

$$(5.32) \quad k = Ae^{-E_a/kt}$$

As noted in Section 3.9, resistance to flow increases as molecular weight increases. Energy and time are required to process polymers into useful items. Increases in energy and time are reflected in an increase in the price of the item and decrease in the lifetime of the equipment used to process the polymers. There is need to produce polymeric materials that exhibit the needed physical properties and yet have a reasonable viscosity to minimize the energy and time required to produce the particular product. Thus, molecular weight control is important.

We have already looked the major indicator of molecular weight control. It is the Carothers' relationship $\overline{DP}_n = 1/(1-p)$ so that chain length can be controlled through extent of reaction and purity of reactants. Thus, the extent of reaction can be controlled through simply stopping the reaction by cooling it. More typically, it is controlled through the use of an excess of one or the other reactant or the introduction of some monofunctional reactant that will halt chain growth when it is added to a growing polymer chain.

For the situation when an excess of one reactant is employed, chain growth continues until all of the reactant that is present in the smaller molar amount reacts leaving chains with end groups derived from the reactant that is present in excess. For a reaction where the number of moles of "B" is in excess, $N_B > N_A$, the extent of reaction for A is p and for B it is " rp " where r is the ratio of N_A/N_B . The following relationship can be derived:

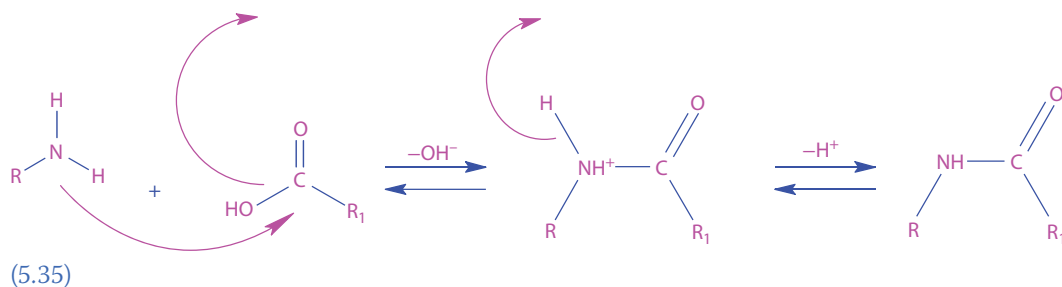
$$(5.33) \quad \overline{DP}_n = \frac{1+r}{1+r-2rp}$$

For an excess in N_B of one mole percent, we have that $r = 100/101 = 0.9901$ and

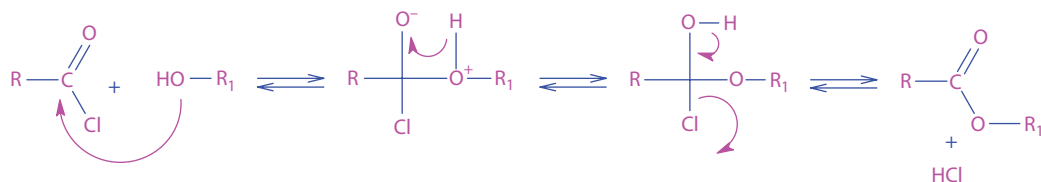
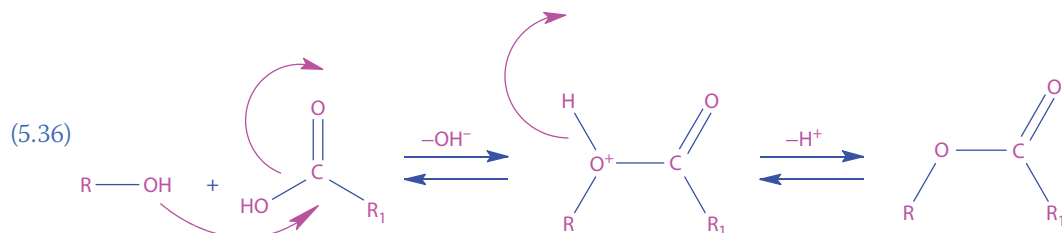
$$(5.34) \quad \overline{DP}_n = \frac{1+0.9901}{1+0.9901-2(0.9901)(1)} = 201$$

5.4 POLYCONDENSATION MECHANISMS

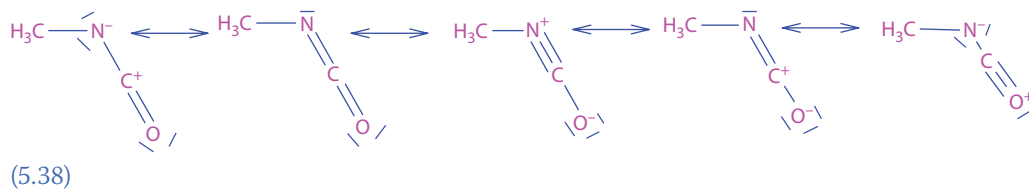
Proposed mechanisms for polycondensations are essentially the same as those proposed in the organic chemistry of smaller molecules. Here, we will briefly consider several examples to illustrate this similarity between reaction mechanisms for small molecules and those forming polymers. For instance, the synthesis of polyamides (nylons) is envisioned as a simple S_N2 -type Lewis acid–base reaction with the Lewis base nucleophilic amine attacking the electron-poor, electrophilic carbonyl site followed by loss of a proton.



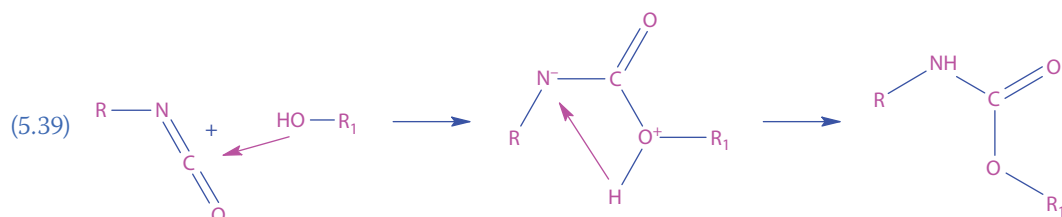
A similar mechanism is proposed for most polyesterifications (5.36 and 5.37).



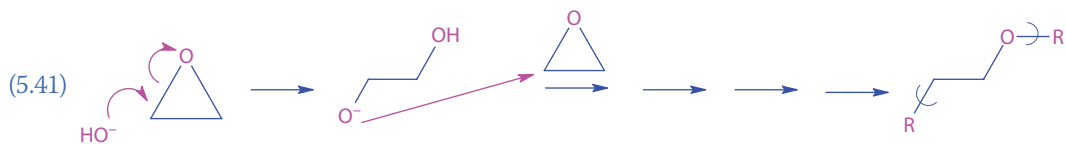
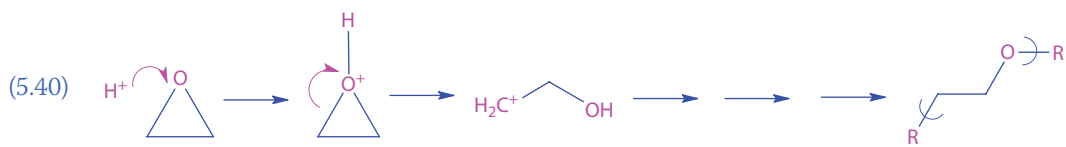
The following are a number of resonance forms for the isocyanate moiety. Because it is surrounded on both sides by atoms, N and O, which have greater electronegativities than the carbon atom, the carbon is electron poor and the site for attack by amines (polyureas) and alcohols (PUs).



PU formation occurs with attack of the nucleophilic alcohol at the electron-poor isocyanate carbon with a proton shift followed by rearrangement to the urethane structure (5.39).



Polyether formation from ring opening forming poly(ethylene oxide) occurs through acid or base catalysis as shown in the following:

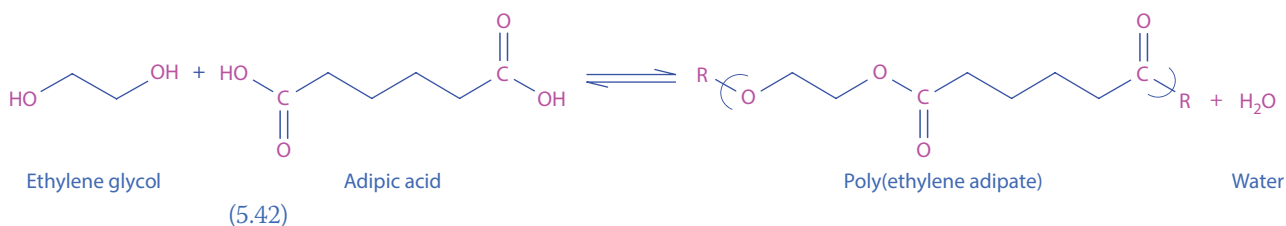


Ethylene oxide is a polar molecule with an excess of electron density on the oxygen making it the site for acid attack, whereas the ethylene moiety is electron poor and the site for nucleophilic attack by the base.

Again, what we have learned from smaller molecule chemistry applies to polymer reactions typically with only modifications that consider the larger size of the polymer.

5.5 POLYESTERS AND POLYCARBONATES

Carothers and his research group at DuPont began to investigate the formation of polymers from the reaction of aliphatic diacids with diols, generally adipic acid and ethylene glycol (derived from reaction of ethylene oxide with water; major ingredient in most antifreeze), in search of materials that would give them fibers. They were only able to form syrupy mixtures. This is because unlike reactions with diamines (Section 5.6), the equilibrium reaction greatly disfavors ester formation. Further, the ability to have almost equal amounts of functional groups is easily achieved with the amines through formation of salts with the amines as shown in Equation 5.54, but diols do not form such salts. The critical need to have the reactants present in equal molar amounts for equilibrium-determined reactions is clearly seen in Equation 5.21. Carothers' group understood the principle of "driving," an equilibrium reaction so sought to remove water thus forcing the reaction toward ester formation. For this, they developed a so-called "molecular still" that was simply heating the mixture and applying a vacuum coupled with a "cold finger" that allowed evacuated water to condense and be removed from the reaction system. Since the fractional conversion (p) was only 0.95, the average chain length of these polyesters was less than 20.



The DuPont research team turned from the synthesis of polyesters to tackle, more successfully, the synthesis of the first synthetic fiber material, nylon, which approached, and in some cases exceeded, the physical properties of natural analogs (next section). The initial experience with polyesters was put to use in the nylon venture. Today, we know that Carothers would have greater success in producing high-molecular-weight polyesters had his group employed transesterification, ring opening (of the "diol" derived moiety), or the reaction of diols with acyl dichlorides (Schotten–Baumann reaction) or anhydrides. These techniques then compose the major techniques employed in the synthesis of polyesters. Each of these reactions involves the nucleophilic addition to the carbonyl group as shown in Section 5.4 and illustrated in Equations 5.36 and 5.37. Focusing on the carbonyl-containing reactant, polyester formation employing direct esterification

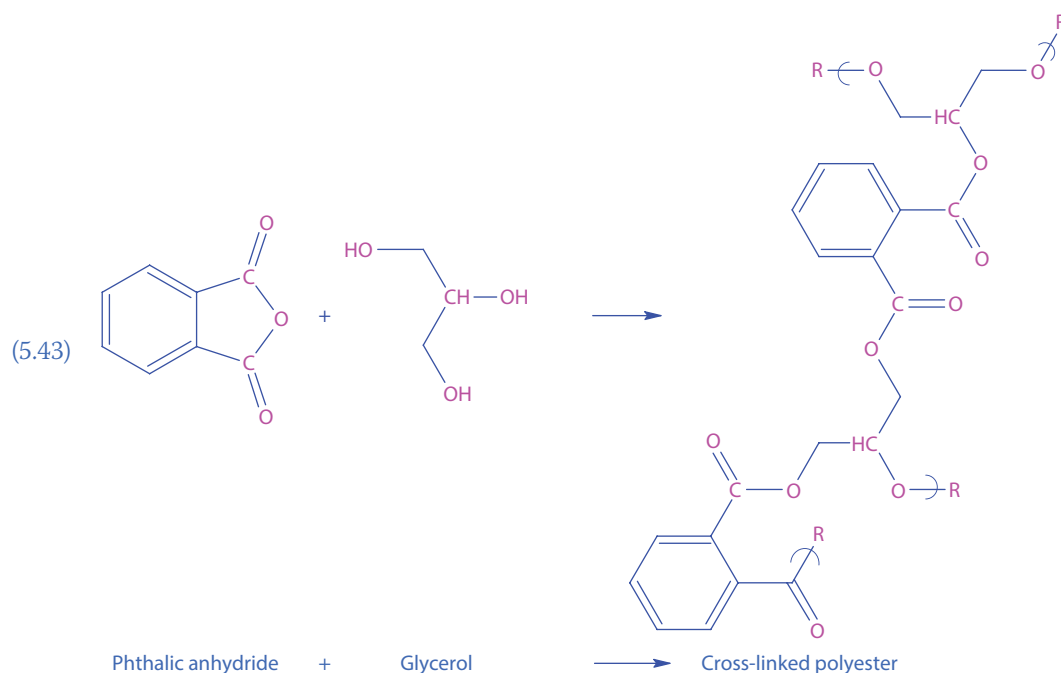
(reaction between an acid and alcohol), and transesterification is relatively slow with each step reversible. Reaction rates are increased through the use of acid catalysts that coordinate the carbonyl oxygen enhancing the electrophilic nature of the carbonyl carbon. Weakly basic catalysts are often employed in transesterification reactions probably to increase the nucleophilicity of the alcohol through formation of an alkoxide ion. Reactions with anhydrides and acid chlorides are more rapid and can occur in an essentially nonreversible fashion. But anhydrides and acid chlorides are considered so-called “high energy” reactants since they often involve additional energy requiring steps in their production and thus are less suitable for large-scale production of materials. The activity energies for direct esterification and transesterification are on the order of 30 kcal/mol (120 kJ/mol), while the activation energies for anhydride and acid chloride reaction with alcohols are on the order of 15–20 kcal/mol (60–80 kJ/mol).

The initial polyester formation actually occurred much earlier and is attributed to Gay-Lussac and Pelouze in 1833 and Berzelius in 1847. These polyesters are called “glyptals” and “alkyds,” and they are useful as coating materials but not for fiber production. While these reactions had low fractional conversions, they formed high-molecular-weight materials because they had functionalities (i.e., number of reactive groups on a single reactant) greater than two resulting in cross-linking.

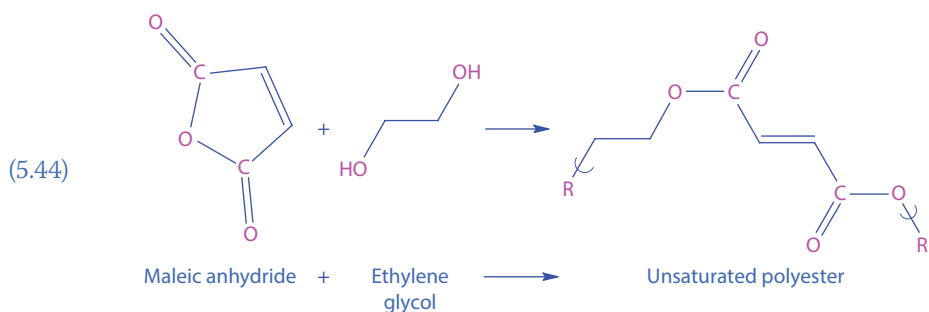
When the average functionality is greater than 2, cross-linking occurs. Glyptal polyesters were produced in 1901 by heating glycerol and phthalic anhydride. Since the secondary hydroxyl is less active than the terminal primary hydroxyls in glycerol, the first product formed at conversions of less than 70% is a largely linear polymer. A cross-linked product is formed by further heating because the functionality of glycerol is three (Equation 5.43).

Alkyds were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils, called drying oils, were transesterified with the phthalic anhydride in the reaction so that an unsaturated polymer was obtained that could later be reacted producing a cross-linked product.

The term alkyd is sometimes used to describe all polyesters produced from polybasic acids and a polyhydric alcohol. The terms saturated and unsaturated polyesters have been used to distinguish between those alkyd polyesters that are saturated from those that contain unsaturation.

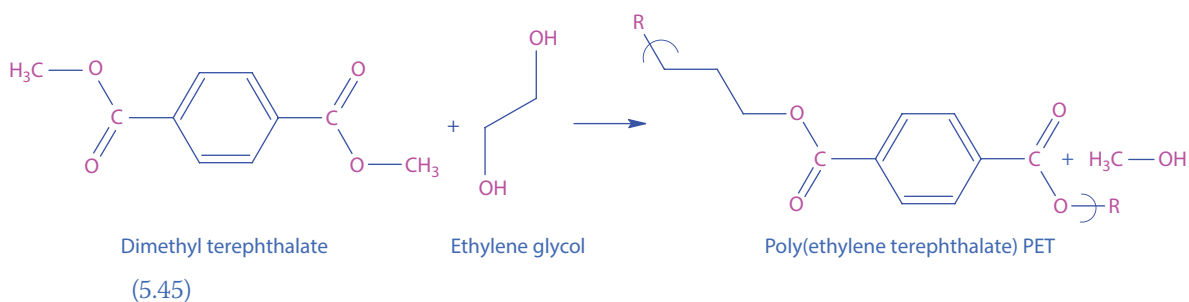


Unsaturated polyesters have been produced from reaction of ethylene glycol with phthalic anhydride or maleic anhydride (Equation 5.44). These polyesters may be dissolved in organic solvents and used as cross-linking resins for the production of fibrous glass-reinforced composites.

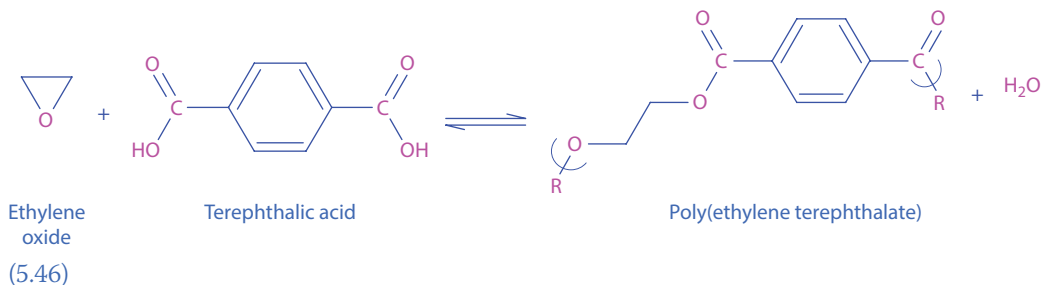


Aromatic polyesters had been successfully synthesized from reaction of ethylene glycol and various aromatic diacids but commercialization awaited a ready inexpensive source aromatic diacids. An inexpensive process was discovered for the separation of the various xylene isomers by crystallization. The availability of inexpensive xylene isomers allowed the formation of terephthalic acid through the air oxidation of the *p*-xylene isomer. DuPont, in 1953, produced polyester fibers from melt spinning, but it was not until the 1970s that DuPont commercially produced polyester fibers.

Expanding on the work of Carothers and Hill on polyesters, Whinfield and Dickson, in England, overcame the problems of Carothers and coworkers by employing an ester interchange reaction between ethylene glycol and the methyl ester of terephthalic acid forming the polyester poly(ethylene terephthalate) (PET) with the first plant coming on line in 1953. This classic reaction producing Dacron, Kodel, and Terylene fibers is shown in the following:



While PET is normally made as described in Equation 5.45, it can also be made from the ring-opening reaction with ethylene glycol as shown in the following:



Polyester, PET, is used in the production of bottles, strapping, sheets and films, and fibers. Polyester fibers (PET; Equations 5.45 and 5.46) are the world's leading synthetic fibers produced at an annual rate of more than 1.5 million tons in the United States. Fibers are produced if the product is pushed through a small hole. As the polyester emerges from the hole, tension is applied assisting the polymer chains to align, giving the fiber additional strength in the direction of pulling. Crystallization of polyester resin can be achieved through heating to about 190°C followed by slow cooling. Rapid cooling, called quenching, produces a more amorphous material from which transparent film is made. Film strength is increased through application of heat and pulling of the film. Biaxially oriented PET film is one of the strongest films available. Thicker film, because of its low carbon dioxide permeability, is used in the manufacture of containers for carbonated drinks through injection molding. It is also used as magnetic film in x-ray and other photographic applications. Thinner film is used in such food applications as food packaging including the boil-in-a-bag foods.

As noted before, PET is employed as both a plastic for making objects as bottles (Picture 5.1) and as a fiber for making clothing, rugs, and other materials. It is used in making carpets employing both spun and filament forms (Picture 5.2). Unlike nylon, PET does not easily stain because it has a greater hydrophobic character. It has good physical characteristics but does tend to “crush” or mat easily.

For clothing, it is often used alone (Picture 5.3) and as a blend with cotton in making a wide variety of clothing items (Picture 5.4).

The major limiting factor in recycling PET bottles is getting people to recycle them. In 2009, only about 30% of the bottles that went onto store shelves were recycled. In the United States, this amounted to almost 1000 million pounds of PET. Many producers have challenged the stores that carry their PET-bottled items to do a better job at recycling. Coca-Cola is committed to recycling



PICTURE 5.1 The two most widely used beverage containers—HDPE (here for milk) and PET or PETE (here for water and soda).



PICTURE 5.2 Portion of a polyester rug.



PICTURE 5.3 Polyester shirts.



PICTURE 5.4 Polyester/cotton blend T-shirts.

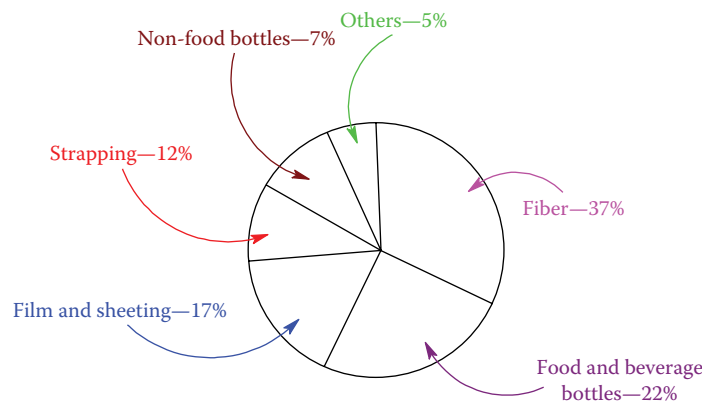


FIGURE 5.6 Fate of recycled poly(ethylene terephthalate) bottles, 2009. (From NAPCOR, National Association for PET Container Resources, Florence, KY.)

50% of their bottles by 2015. About 60% of the recycled bottles are turned into fiber and new bottles (Figure 5.6).

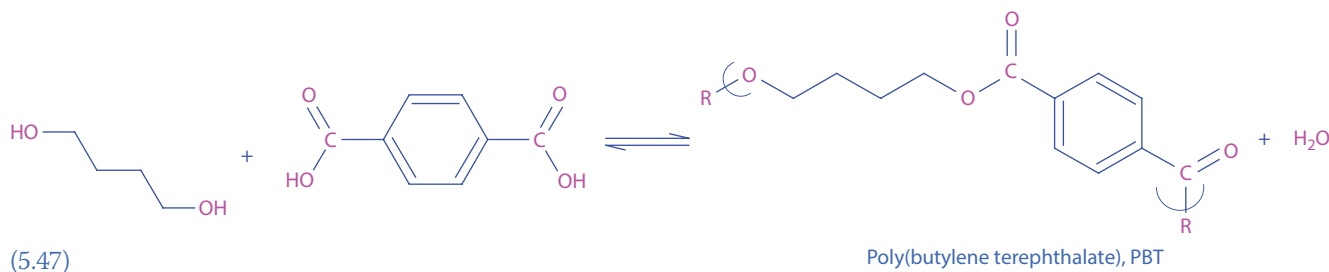
There is an interesting problem occurring with PET recycling. Some manufacturers are including additives intended to help in the degradation of PET but making ready recycling more difficult. Also, the presence of these additives limits the number of times that PET can be recycled.

The end users of many materials are helping drive the move toward more “green” materials. Coca-Cola and Pepsi, the major users of PET-derived bottles, are both working to increase the use of bio-derived materials. Since 2009, Coca-Cola has been using a bottle called the PlantBottle for their Coca-Cola soft drink and Dasani water bottles. Most of the bottle makers are part of this effort. H.J. Heinz is now packaging their ketchup in PlantBottles. The PlantBottle is formed from petroleum-based terephthalic acid and biobased ethylene glycol. There are various procedures employed to create the biobased ethylene glycol. Currently, the major avenue is to dehydrate bio-derived ethanol forming ethylene that is converted into ethylene oxide and then to ethylene glycol. The move toward a 100% biobased PET awaits a ready avenue to synthesize terephthalic acid via a biological route.

Scale and sustainability are two important aspects. Coca-Cola, alone, produces more than 100 billion bottles yearly. Included in all of this is cost. As the supply lines and amounts increase, there will be some cost reduction. Supply will increase as additional feedstocks become reasonable for the production of biobased materials. While many sources are sugar and starch-intense, this will shift since it is limited and competes for food uses. Much of the experimental and start-up efforts are being done in conjunction with partnerships with smaller firms that have expertise in biobased production and conversion of materials.

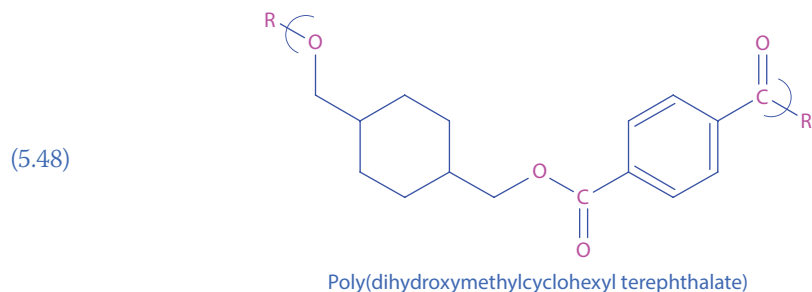
PET is difficult to mold because of its high melting, T_m 240°C, point. PET also crystallizes relatively slowly so that extra care must be exercised to insure that the PET-molded products are fully crystallized or the partial crystallized portions will be the preferred sites for cracking, crazing, shrinkage, etc. Thus, nucleating agents and crystallization accelerators have been used to improve the crystallization rate. Post annealing has been used where appropriate.

Poly(butylene terephthalate) (PBT) (5.47), because of the addition of two methylene units in the diol-derived portion, is lower melting than PET with a T_g of about 170°C. Moldability of aryl polyesters has been improved through the use of PBT instead of PET or by use of blends of PET and PBT. These aryl polyesters are used for bicycle wheels, springs, and blow-molded containers.



By comparison to PET, PBT melts at a lower temperature and crystallizes more rapidly and is often employed as a molding compound. PBT offers a balance of properties between nylons and acetals with low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the trade name Celanex. A PBT molding compound was first sold under the trade name Valox. Today, there are many PBT molding compounds available.

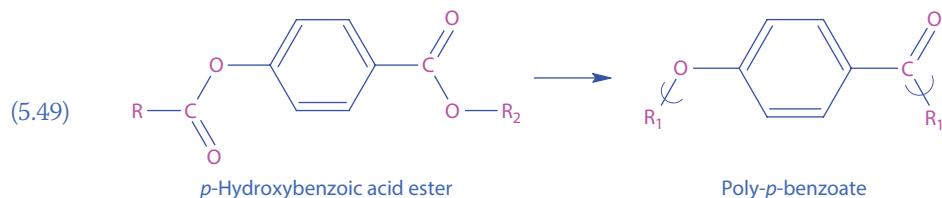
Poly(dihydroxymethylcyclohexyl terephthalate) (5.48) was introduced by Eastman Kodak as Kodel in 1958. In comparison to PET and PBT, the insertion of the cyclohexyl moiety gives a more hydrophobic material as well as a more moldable product that can be injection molded. The sole raw material is again dimethyl terephthalate. Reduction of the dimethyl terephthalate gives the dialcohol cyclohexanedimethanol. (Notice the reoccurring theme of reusing or using in a modified form the same readily available and inexpensive materials.) This material, along with blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to package hardware and other heavy items as well as blow molded to produce packaging for shampoos, liquid detergents, etc.



The hard–soft block copolymer approach employed to produce segmental PUs (Sections 5.9 and 8.4) has also been used with polyesters with the hard block formed from 1,4-butanediol and terephthalic acid while the soft block is provided from oligomeric (approximate molecular weight of 2000 Da) poly(tetramethylene glycol) and is sold under the trade name Hytrel.

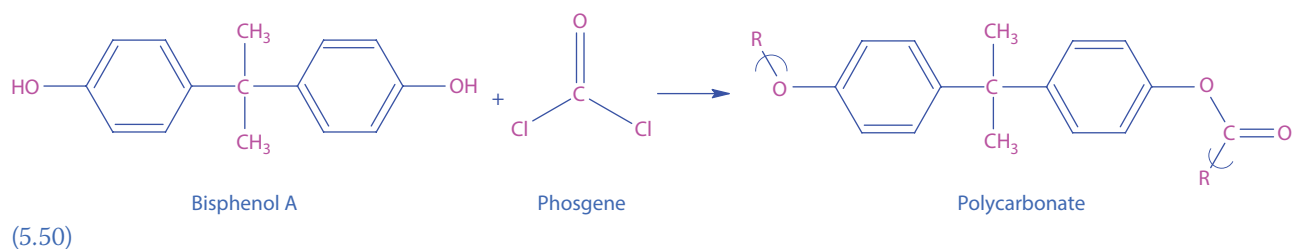
Along with nylons, polyester fibers approach and exceed common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Blended textiles from polyester and cotton and wool also can be made to be permanent press and wrinkle resistant. The fibers are typically formed from melt or solvent spinning. Chemical and physical modification is often employed to produce differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials with differing shrinkage properties. Different shaped dyes produce materials with varying contours and properties including hollow fibers.

Several “wholly” aromatic polyesters are available. As expected, they are more difficult to process and stiffer, less soluble, but are employed because of their good high thermal performance. Ekonol is the homopolymer formed from *p*-hydroxybenzoic acid (Equation 5.49). Ekonol has a T_g in excess of 500°C. It is highly crystalline and offers good strength.



It is not unexpected that such aromatic polyesters have properties similar to polycarbonates because of their structural similarities.

Polycarbonates were originally produced from the interfacial polymerization reaction of phosgene with bisphenol A (BPA) [2,2'-bis(4-hydroxyphenyl) propane] (Equation 5.50). It is an unusually tough and transparent plastic available under the trade names Lexan (General Electric) and Merlon (Mobay). Polycarbonates can also be made from the ester interchange between diphenyl carbonate and BPA. The melting point of polycarbonates is decreased from 225°C to 195°C when the methyl pendant groups are replaced by propyl groups.



Polycarbonates and polycarbonate-polyester copolymers are used for glazing, sealed beam headlights, door seals, popcorn cookers, solar heat collectors, and appliance housings.

Prerecorded compact discs (CDs) are made of rigid, transparent polycarbonates (such as Equation 5.50) with a reflective metal coating on top of the polycarbonate. A laser is used to encode information through creation of physical features sometimes referred to as “pits and lands” of different reflectivity at the polycarbonate-metal interface. Thus, CDs are part of our audio revolution that started in the 1800s and now has become part of our Wi-Fi revolution with streaming, etc. (Picture 5.5).

Recordable CDs contain an organic dye between the polycarbonate and metal film. Here, a laser creates areas of different reflectiveness in the dye layer through photochemical reactions.

A beam from a semiconductor diode laser “interrogates” the undersides of both types of CDs seeking out areas of reflected, corresponding to the binary “one,” and unreflected, corresponding to the binary “zero,” light. The ability to “read” information is dependent on the wavelength of the laser. Today, most of the CD players use a near-infrared laser because of the stability of such lasers. Efforts are underway to develop stable and inexpensive lasers of shorter wavelengths that will allow holding of more information within the same space.

There is concern that BPA may cause neural and behavioral changes in infants and children. A major line of exposure to infants is in baby bottles. In our modern age, the composition of baby bottles had evolved from glass to polyethylene to polycarbonates and now back to glass and other newer materials such as Tritan that is a proprietary copolyester developed by Eastman with properties similar to polycarbonate. While the use of most polycarbonates will continue, the “better to be safe than sorry” motto is best used for infants that are more susceptible than adults to various agents.

Another somewhat recent addition to the polyester market is poly(trimethylene terephthalate) (5.51) also called Sorona or 3GT. It is advertized as a green material since the 1,3-propanediol is obtained from the fermentation of corn. A recent addition to the carpet

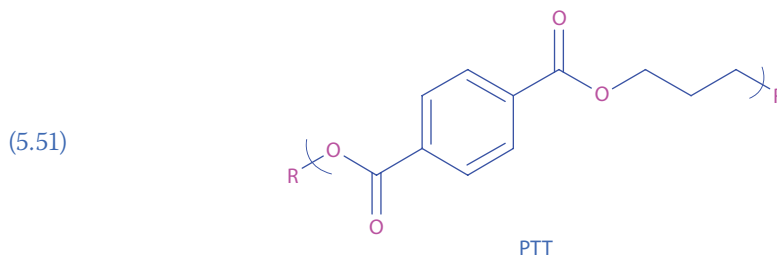


PICTURE 5.5 Audio recordings from late 1800s to current.



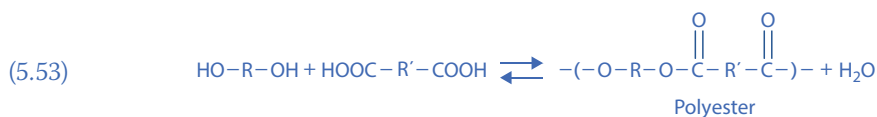
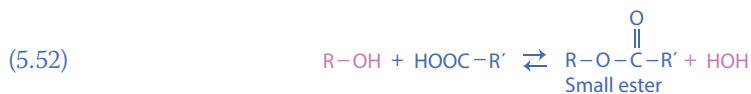
PICTURE 5.6 Rug made from corn-derived material.

market is formed from poly(trimethylene terephthalate) and marketed under the trade name Triexta (Picture 5.6).



5.6 SYNTHETIC POLYAMIDES

Wallace Hume Carothers was brought to DuPont because his fellow researchers at Harvard and the University of Illinois called him the best synthetic chemist they knew. He started a program aimed at understanding the composition of natural polymers such as silk, cellulose, and rubber. Many of his efforts related to condensation polymers were based on his belief that if a monofunctional reactant reacted in a certain manner forming a small molecule (5.52) that similar reactions except employing reactants with two reactive groups would form polymers (5.53).



While the Carothers' group had made both polyesters and polyamides, they initially emphasized work on the polyesters since they were more soluble and easier to work with. One of Carothers' coworkers, Julian Hill, noticed that he could form fibers if he took a soft polyester material on a glass stirring rod and pulled some of it away from the clump. Because the polyesters had too low softening points for use as textiles, the group returned to work with the polyamides. They found

that fibers could also be formed by the polyamides similar to those formed by the polyesters. These polyamides allowed the formation of fibers that approached and, in some cases, surpassed the strength of natural fibers. This new miracle fiber was introduced at the 1939 New York World's Fair in an exhibit that announced the synthesis of this wonder fiber from "coal, air, and water"—an exaggeration—but nevertheless eye catching. When the polyamides, nylons, were first offered for sale in New York City, on May 15, 1940, nearly 800,000 pairs were sold in the first few hours. Nylon sales took a large drop when it was noted that nylon was needed to produce the parachute material so critical to World War II.

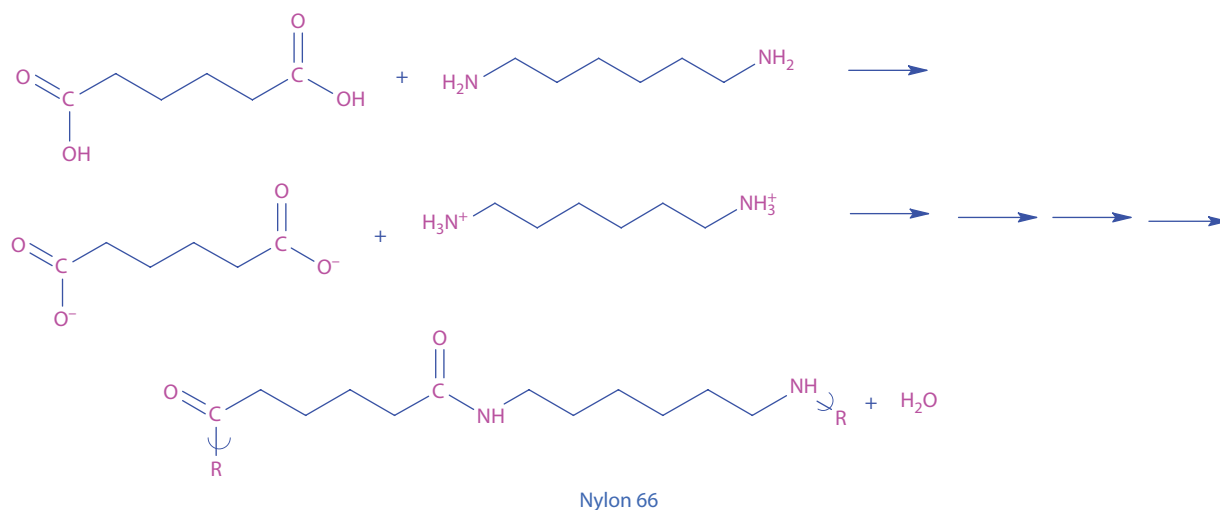
The first polyesters produced by Carothers had relatively low molecular weights because of low fractional conversions. Carothers was successful in producing higher-molecular-weight polymers by shifting the equilibrium by removing the water produced. Equation 5.53 is an equilibrium process with the removal of water driving it toward polymer formation. However, these aliphatic polyesters, which he called "super polymers," lacked stiffening groups in the chain and thus had melting points that were too low for laundering and ironing.

Carothers' next step was to move from polyesters to nylons and to increase the fractional conversion (p) by making salts by the equivalent reaction of 1,6-hexanediamine (hexamethylenediamine) and adipic acid. These salts were recrystallizable from ethanol giving essentially a true 1:1 ratio of reactants. Thus, a high-molecular-weight polyamide generally known as nylon, in this case nylon 66, with a melting point of 265°C was produced from the thermal decomposition of this equimolar salt as shown in Equation 5.54.

Since the molecular weight of this nylon 66, produced by Carothers, was higher than he desired, he added 1% acetic acid (a monofunctional acid that acted to terminate chain growth) that produced a lower molecular weight nylon 66 with a melting point of about 200°C.

While nylon 66 was chosen to be the flagship polyamide, some of its properties were inferior to other nylons initially studied. Nylon 66 was chosen because each of the reactants, the diacid and diamine, had six carbons in it. Carothers and DuPont reasoned that they could find synthetic routes from the six-carbon benzene that was available in large amounts from coal through coke oven distillation or from coal tar, where benzene was a by-product of heating coal for the steel industry. Thus, the industrial theme of having readily available inexpensive large quantities of the starting materials was a deciding factor in choosing to focus on nylon 66.

Molded nylon 66 is used for lawn mower blades, bicycle wheels, tractor hood extensions, skis for snowmobiles, skate wheels, motorcycle crank cases, bearings, and electrical connections. Fiber nylon 66 is used in clothing, fabrics, and rugs. As a rug or carpet, it is either dyed topically or in its molded state. It can be easily printed and has outstanding wear properties (Picture 5.7). Unfortunately, nylon 66 carpets stain easily but most have an antistaining agent added.



(5.54)

In the early 1950s, George deMestral was walking in the Swiss countryside. When he got home, he noticed that his jacket had a lot of cockleburs on them. For some reason, he examined the



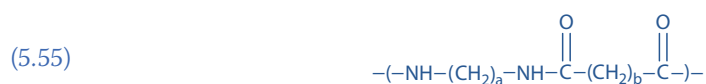
PICTURE 5.7 Portion of a nylon rug.



PICTURE 5.8 Light weight nylon jacket using both zipper and hook and eye systems for closure.

cockleburs and noticed that they had a lot of tiny “hooks.” His cotton jacket had loops that “held” the cockleburs. He began putting into practice his observations, making combinations of materials with rigid hooks and flexible loops or eyes. The initial hook and eye for commercial use was made in France. Today, Velcro, the name given to the hook-and-eye combination, is often based on nylon as both the hook and eye material. Remember that nylon can be made to behave as both a fiber and as a plastic. Polyester is blended with the nylon to make it stronger. Polyesters have also been employed to make hook-and-eye material. The hook-and-eye material is used to fasten shoes and close space suits and in many other applications (Picture 5.8).

The general structure for aliphatic nylons for naming purposes is



where

a is the number of carbons derived from the amine-associated portion

b is the number of carbons, including the carbonyl carbon atoms, associated with the diacid

Thus, nylon 66 has 6 carbons derived from hexamethylenediamine, a is 6, and b is 6 for the carbons derived from adipic acid that includes two carbonyl carbons as well as four methylene carbon atoms. It is of interest that nylon 66 is also written as nylon 66 and nylon 66.

Nylon 6,10 is derived from hexamethylenediamine and sebacic acid (dodeconic acid) and is more resistant to moisture and more ductile than nylon 66 because of the presence of the additional flexible nonpolar methylenes. The properties of these polyamides are improved by the formation of polyether blocks (NBC) and by blending with thermoplastics such as EPDM, PET, PBT, and TPE. NBC (Nyrin) is more expensive than reaction injection molded (RIM) PU, but it can be heated to 200°C without melting. NBC moldings are produced from the RIM of poly(propylene glycol) and caprolactam. The tendency of these moldings to swell in water is reduced by reinforcing them with fibrous glass.

Nylon 6 (5.56) structurally quite similar to nylon 66 was initially produced in Germany by the ROP of caprolactam partly as a way to avoid the patents established by DuPont a decade before. The copolymer of nylon 6 and nylon 66 has a smoother surface than either of the homopolymers.



Nylon 66 is the dominant (sales wise) nylon in the United States while nylon 6 is the dominant nylon in Europe.

Carothers and his group had considered a number of routes to produce the polyamides including 6-aminocaproic acid. In their attempts to form nylon 6 from 6-aminocaproic acid, they obtained a waxy material that they believed to be oligomeric polyamide along with a cyclic material. The cyclic material was caprolactam. Carothers published the results noting that this cyclic amide could not give polyamides. This paper cost DuPont a lot of money because chemists at I.G. Farben scoured the literature looking for ways to break DuPont's hold on the production of nylon 66 because any company using nylon 66 had to pay royalties to DuPont. This paper appeared to galvanize efforts at I.G. Farben to polymerize caprolactam. They thought that the "secret" was the presence of a little water that allowed the decyclization of caprolactam forming nylon 6. Incidentally, caprolactam was the same product that Beckmann produced in his reaction with oximes years before in 1886.

Interestingly, the ROP of caprolactam occurs via a chain process producing a "condensation product," an exception to the typical route to condensation polymers.

One of the initial reports indicating that DuPont was focusing their efforts on polyamides appeared in *Time* magazine, September 14, 1931, where appeared "By heating castor oil with an alkali and mixing the results with motor antifreeze.... DuPont chemists produced an artificial silk fiber." The article continued to note that while they had accomplished this feat, the process was too expensive to be commercially viable. The article was based on papers given by Carothers at a recent American Chemical Society in Buffalo, NY, the previous month titled "Castor Oil Silk."

Nylon-11 is produced from ricin, a protein present in Caster beans. The original sequence is described in Figure 5.7. Today, there exist a number of synthetic sequences including having the Caster oil feedstock treated with methanol giving methyl ricinoleate that is converted to 11-aminoundecanoic acid, which is then polymerized at 200°C giving nylon-11.

Nylon-11 has excellent electrical properties and is used in mechanical engineering for moving components such as bearings and gears. It is also used in the manufacture of hydraulic and pneumatic hoses, fuel lines, and flexible teeth for harvesting machinery and in the soles of soccer shoes and as transparent sheets (Picture 5.9) and films.

The ability to form strong hydrogen bonding is reduced, and the flexibility increased, by placing bulky methoxymethyl pendent onto nylons (5.57).

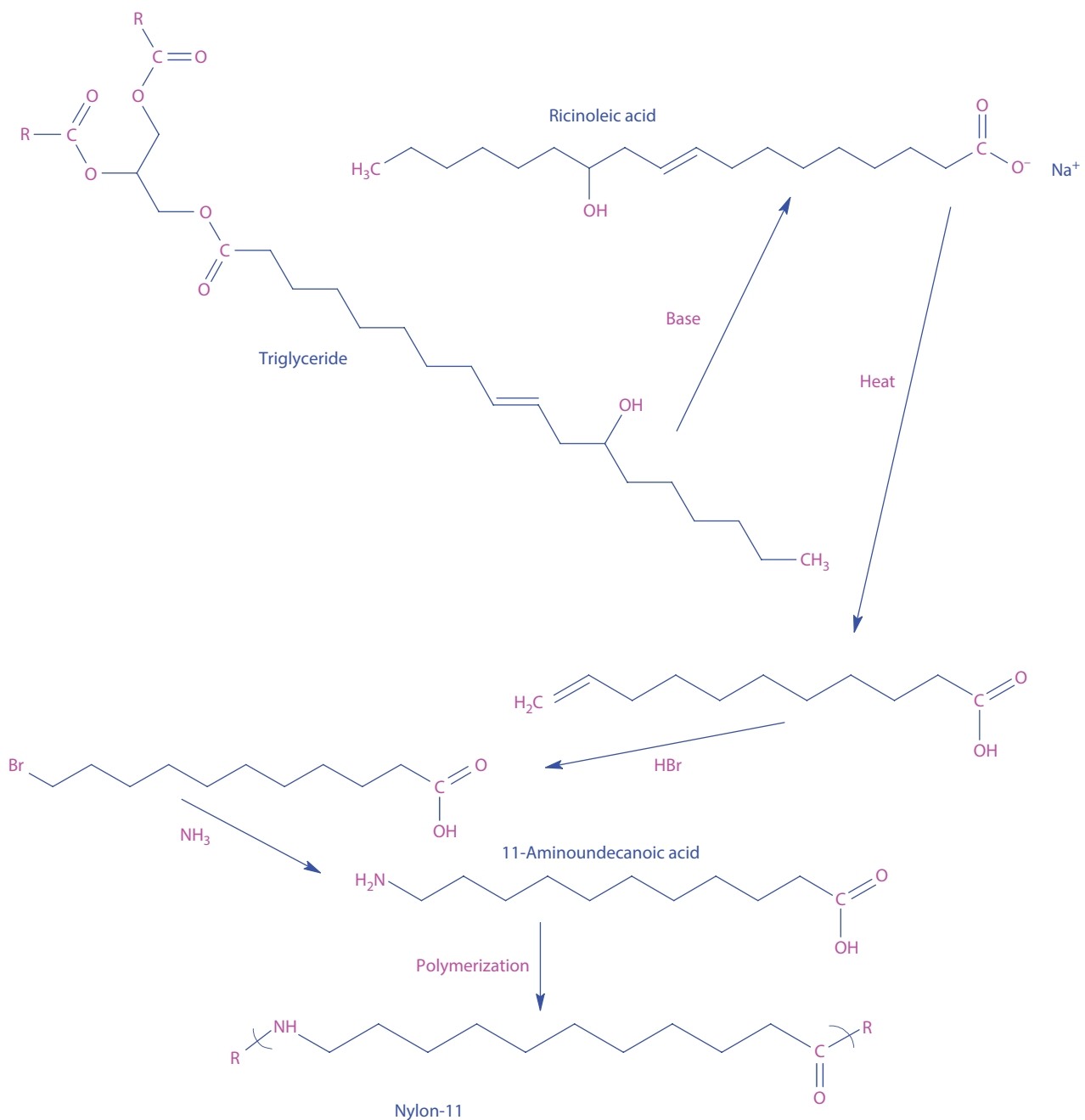
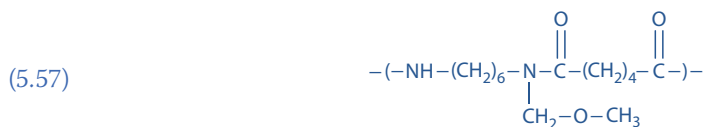
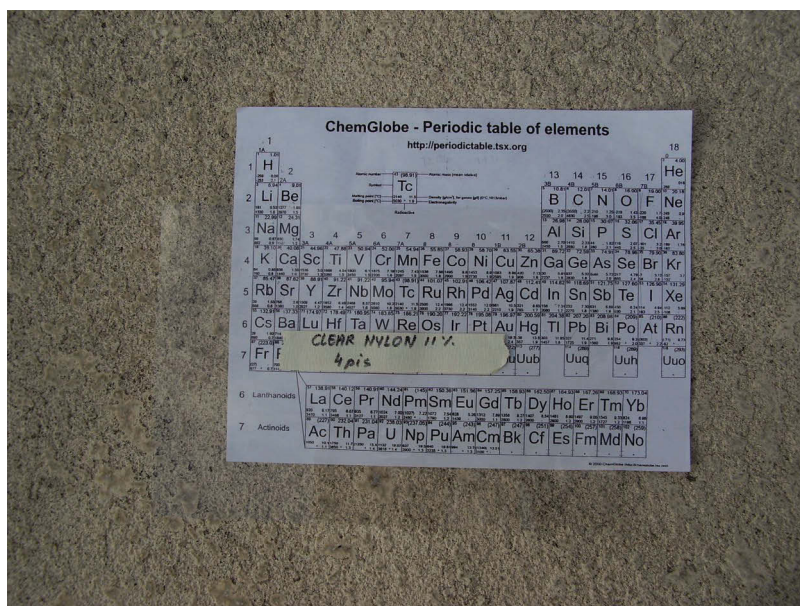


FIGURE 5.7 Synthesis of nylon-11 from triglycerides derived from the castor bean.



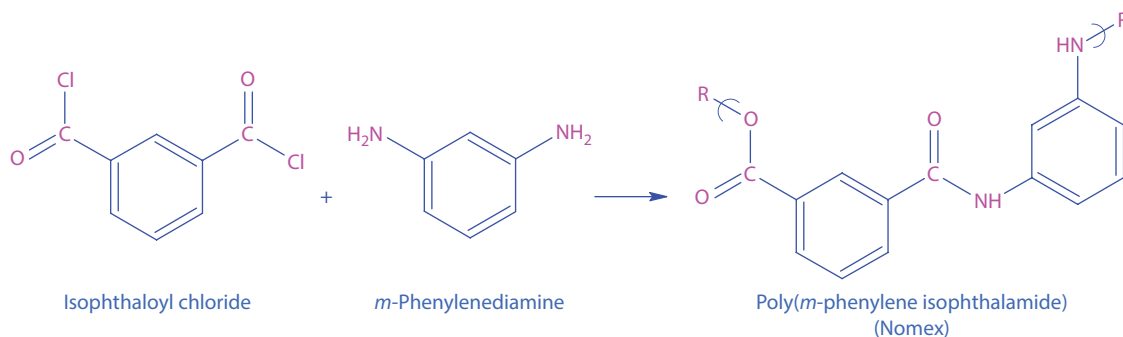
While aliphatic-containing polyamides are given the name nylons, those where at least 85% of the amide groups are attached to an aromatic are called “aramids.” Aramids are stronger and tougher than nylons but they are also more difficult to solubilize and fabricate. Because the presence of the aromatic groups causes the aramids to be stiff, they often form liquid crystals (LCs) that are present in a nematic LC state in concentrated solution.



PICTURE 5.9 Clear sheet of nylon-11 polymer covering a periodic table.

Aramids are generally prepared by the solution or interfacial polycondensation of meta- and para-substituted diacid chlorides and/or diamines. In some systems, synthesis is achieved under rapidly stirred conditions where the polymer is quasi-soluble in the system. The polymer mixture is forced through a small opening into a nonsolvent forming a fiber without the need to dissolve the polymer before fiber formation.

Poly(*m*-phenylene isophthalamide) (5.58), sold under the trade name Nomex, exhibits good thermal stability decomposing above 370°C.



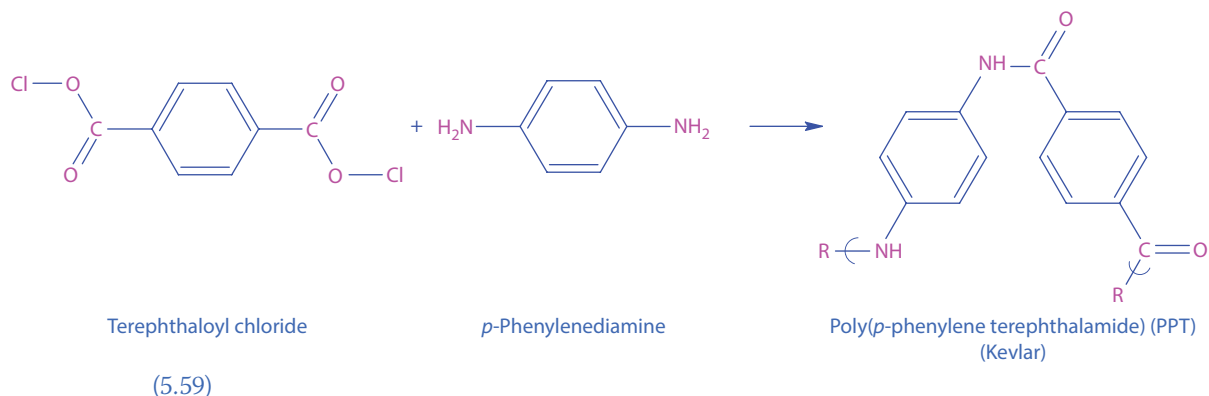
(5.58)

Nomex is sold as both a fiber and sheet. The sheet material is often a laminate with paper and used in electrical applications such as circuit boards and transformer cores. Firefighter gear generally includes a Nomex hood to protect the face not protected by the helmet. Race car drivers are required to wear flame-resistant underwear, balaclava, socks, shoes, and gloves that are typically made from Nomex fiber. Military pilots also wear flight suits that are Nomex.

Because of the meta-orientations of the reactants, Nomex chains do not realign on fiber formation resulting in a material that is weaker than the corresponding para-oriented polymer, Kevlar.

The corresponding aramid produced using the para reactant in place of the meta gives poly(*p*-phenylene terephthalamide) (PPT) produced under the trademark Kevlar and developed by DuPont by Stephanie Kwolek and Roberto Berendt in 1965 (5.59). Like Nomex, Kevlar exhibits good thermal stability decomposing above about 500°C. Because of its outstanding strength, it was used as the skin covering of the Gossamer Albatross that was flown, using only

human power, across the English Channel. Aramids are also used as fiber reinforcement in composites and as tire cord.



Kevlar fiber has a high tensile strength (about 3000 MPa) and a relatively low density (about 1.4 g/mL) leading to the often used statement that Kevlar is five times stronger than steel (on an equal weight basis). It gains part of its strength from the interchain hydrogen bonds formed between the carbonyl groups and hydrogen atoms on amines on neighboring chains and on the partial stacking of the phenylene rings allowing pi-pi interactions between the members of the stacking units. The molecularly rigid chains tend to form sheetlike structures similar to those of silk.

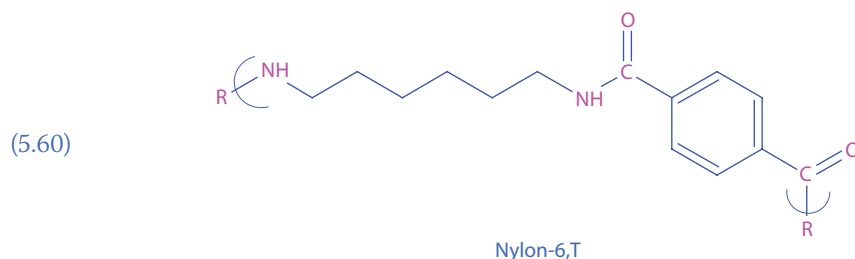
Kevlar is used in the manufacture of the so-called “bulletproof” clothing used by the military, policemen, and SWAT teams. In truth, most bulletproof clothing is bullet resistant and unless quite bulky not able to “stop” most rifle bullets or high caliber hand guns. It is also used in the construction of bullet-resistant facemasks by the military and by motorcycle riders to protect against abrasion.

There are many other commercial uses for Kevlar. It is used as the inner liner for some bicycle tires to protect against puncture. It is also being used for bow strings in archery. Drumheads have been made from Kevlar. Kevlar is widely employed as the protective outer sheath for fiber optic cable and as the reinforcing layer in rubber bellow expansion joints and hoses for high-temperature applications.

Aramid materials are also employed in the U.S. space program along with other “space-age” materials. The thermal micrometeoroid garment on the Extravehicular Mobility Unit, Advanced Crew Escape Suit, thermal blankets, and the fuselage, bay doors, upper wind surfaces of the Space Shuttle Orbiter employs Nomex, Kevlar, and Gore-Tex materials. The airbags for the Mars Pathfinder and MER rovers, the Galileo atmospheric probe and the new Crew Exploration Vehicle all have aramid materials. Aramid materials are used in the form of thin pads to protect sintered silica-fiber mats from stress and vibrations during the flight of the space shuttle.

Aramid fibers are widely employed in the construction of composites where high strength is required. The continuous phase is often an epoxy resin. Applications include cricket bats, helicopter rotor blades, bodies for formula one race cars, kayaks, tennis rackets, lacrosse sticks, and ice hockey sticks.

Several so-called semi-aromatic nylons have been produced. Nylon 6,T is produced from condensation of terephthalic acid and 1,6-hexanediamine (5.60). Both reactants are readily available and inexpensive, and the resulting materials offer greater strength than simply wholly aliphatic nylons such as nylon 66. Nylon 6,T has a very high T_m of 370°C and a T_g of 180°C. The high T_m results in the need for a high temperature to be employed in processing so that a third reactant is often introduced to lower the T_m and the processing temperature. “Third reactants” often used are adipic acid, caprolactam, isophthalic acid, and 1,5-hexyl diamine. These materials are sold under the trade names Zytel HTN, Ultramid T, and Amodel R.



Nylons offered new challenges to the chemical industry. Because of the presence of polar groups, the attractive forces between chains were high in comparison to vinyl polymers. Nylons are generally semicrystalline, meaning they have a good amount of order. While they have a T_m , the main physical transition is the T_g so that they undergo a sharper transition from solid to melt in comparison to many of the vinyl polymers discussed in the next three chapters. Thus, the processing temperature window is narrower. If melt flow is required for processing, then the temperature must be sufficient to allow for ready flow but low enough so as not to break primary bonds within the processed material. Even so, processing techniques have been developed that allow nylons to be readily processed using most of the standard techniques.

Since chains of nylons having an even number of carbon atoms between the amide and acid groups pack better, often their melting points are higher than comparable nylons with odd numbers of carbon atoms. Further, the melting points decrease and the water resistance increases as the number of methylene groups between the amide and acid groups increases.

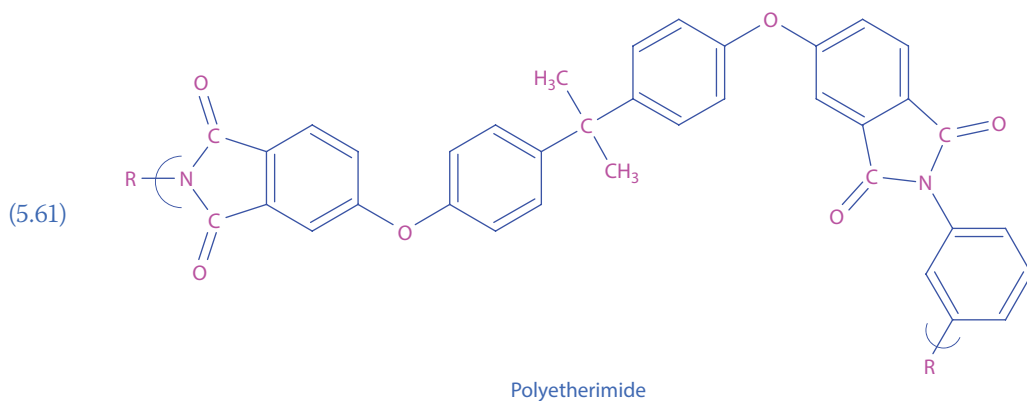
The presence of the polar groups results in materials with relatively high T_g and T_m values so that unlike most vinyl polymers that must be above their T_g to allow needed flexibility, nylons, and many condensation polymers function best where strength, and not flexibility, is the desired behavior. Because of the presence of these polar groups, which also allow for hydrogen bonding, nylons and most condensation polymers are stronger, more rigid and brittle, and tougher in comparison to most vinyl polymers. Nylons are also “lubrication-free” meaning they do not need a lubricant for easy mobility so that they can be used as mechanical bearings and gears without the need for periodic lubrication.

In general, more crystalline nylons are used as fibers while less crystalline nylon materials are more used as plastics. The amount of crystallinity is controlled through a variety of means including introduction of bulky groups and asymmetric units, rapid cooling of nonaligned melts, and introduction of plasticizing materials. The theme of using asymmetric units was used by Grace and Company in developing Trogamid T, an amorphous transparent nylon, from the condensation of terephthalic acid with a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamines.

5.7 POLYIMIDES

The initial announcement for the commercial preparation of polyetherimides (PEIs) was made by General Electric in 1982 under the trade name Ultem. The final reaction involves the imidization of a diacid anhydride through reaction with a diamine, here *m*-phenylenediamine (5.61). The “ether” portion of the polymer backbone results from the presence of ether linkages within the diacid anhydride.

Utem is used in medical and chemical instrumentation. Products made from Utem are high melting, offer good stiffness, transparency, impact and mechanical strength, high flame resistance, low smoke generation, and broad chemical resistance. Some of these properties are expected. The high flame resistance is at least in part derived from the presence of already partially or largely oxidized atoms in the product. The low smoke generation is partially derived from the largely cyclic structure with other cyclic structures predictable from the product structure if exposed to sufficient heat. These cyclic structures often give products that are stable when the material is exposed to ordinary flame conditions.

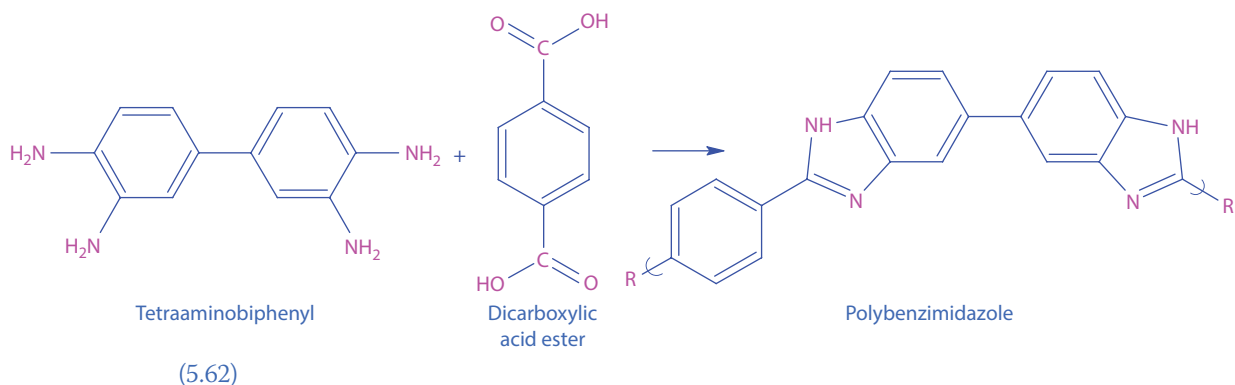


The general good mechanical properties are a result of the presence of strong double bonds present within polycyclic structures composing the polymer backbone plus the presence of strongly polar bonding units that allow the formation of good interactions between chains. Further, the structure is largely rigid with good dimensional stability along the polymer backbone. Any flexibility is gained largely from the presence of the ether linkages for the PEIs and the presence of methylene units for the polyimides. These products offer good stable melt viscosities even after recycling several times. They can be processed using a variety of techniques including formation of sections as thin as 5 miles (1 mile = 0.001 in.).

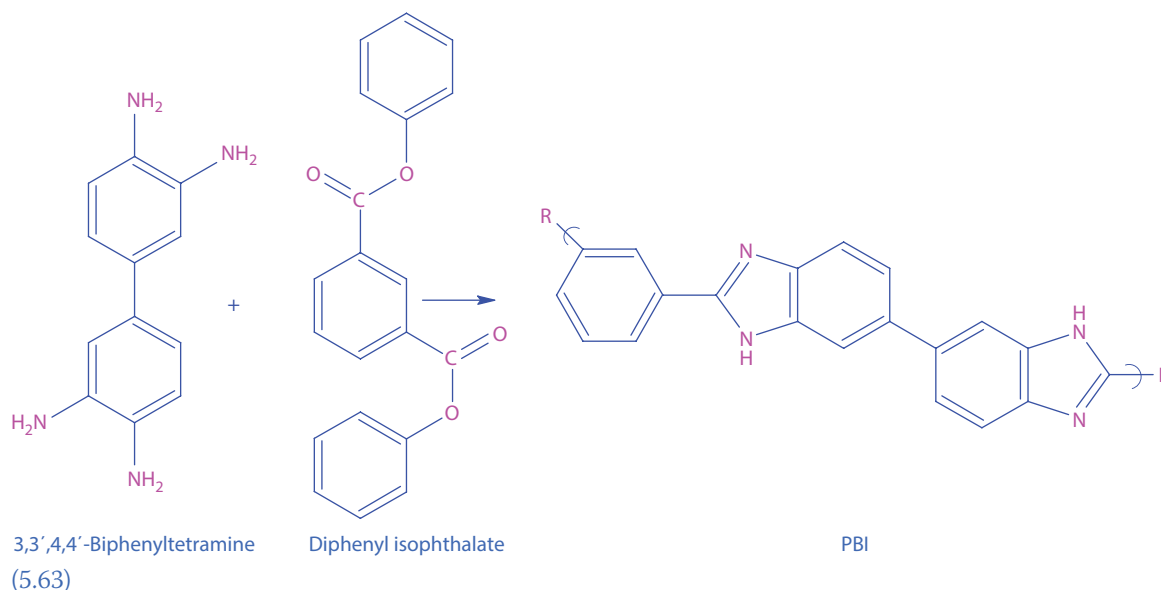
While Ultem is an example of thermoplastic polyimides, there are a number of thermoset polyimides. These are known for good chemical resistance and mechanical properties as well as good thermal stability. They are employed in electronic applications as insulating film on magnetic wire, for flexible cables, and for medical tubing. On a laptop computer, the cable connecting the main logic board to the display is often a polyimide with copper conductors. Polyimides are also used as high-temperature adhesives in the semiconductor sector.

5.8 POLYBENZIMIDAZOLES AND RELATED POLYMERS

Many heterocyclic polymers have been produced in an attempt to develop high-temperature-resistant polymers for aerospace applications. Among these are the polybenzimidazoles (PBIs), which, as shown in Equation 5.62, are prepared from aromatic tetramines and esters of dicarboxylic acids, here terephthalic acid. In standardized procedures, the reactants are heated to below 300°C forming soluble prepolymer, which is converted to the final insoluble polymer by further heating.

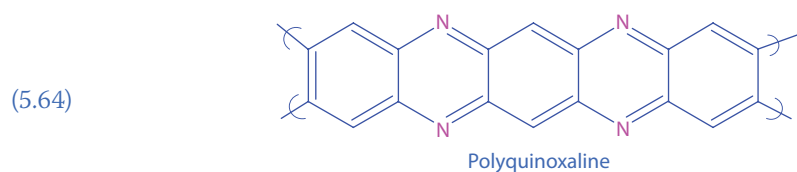


PBI fiber has an extremely high melting point and does not ignite. They were initially made under the supervision of Carl Shipp “Speed” Marvel before 1983 as part of an overall project for the U.S. Air Force to create aerospace material. Celanese first produced PBI fibers (5.63) in 1983 from reaction between tetra-aminobiphenyl and diphenyl isophthalate. This structure is analogous to that given in (5.62).



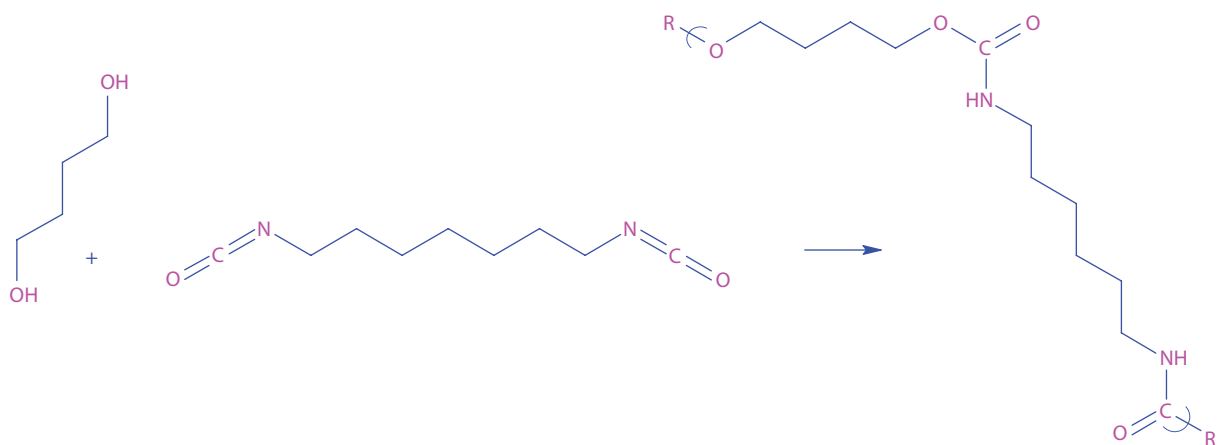
PBI fibers are employed in the production of firefighter coats and suits, high-temperature gloves, welders, astronaut space, and race driver suits.

Polymers, such as PBI, have weak links in them since there are present single bonds within the polymer backbone. This weakness is overcome by the synthesis of ladder polymers, such as polyquinoxaline (Equation 5.64), which have two covalent bonds throughout the chain. Thus, the integrity of the polymer is maintained even if one bond is broken.



5.9 POLYURETHANES AND POLYUREAS

PUs, or polycarbamates, were first made by Bayer and coworkers in 1937 reacting diols and diisocyanates. This monomer combination avoided conflict with existing patents by Carothers and DuPont related to polyester production. The development of PUs was stunted because of their use as aircraft coatings in World War II. In 1952, they became commercially available. The PU shown in Equation 5.65 is sold under the trade name Perlon U. As in the case with nylons and polyesters, higher melting products are often formed when the number of carbon atoms is even since this allows a closer packing of the chains.



Isocyanates react with water producing unstable carbamic acids that decompose forming diamines and carbon dioxide. This forms one basis for the production of PU foams. Thus, isocyanate-terminated PUs are formed that, when exposed to moisture, form foams.

Many PUs are based on aromatic diisocyanates such as toluene diisocyanate (TDI) (5.66) that impart chain stiffness into the PU. PU foams are used in bedding, pillows (Picture 5.10), furniture, automotive seating, and carpet backing.

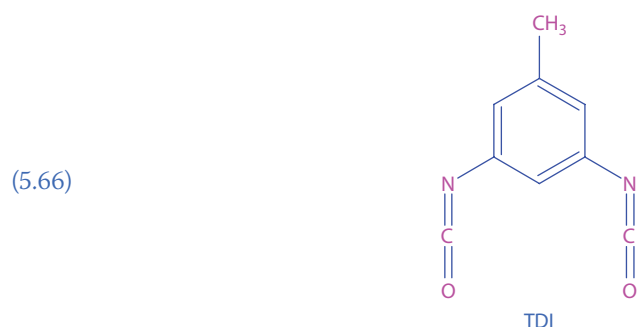
Cross-linked PU coatings, elastomers, and foams can be produced using an excess of the diisocyanate, which reacts with the urethane hydrogen producing an allophanate, or incorporating polyols such as glycerol in the reaction mixture. Larger polyols called macroglycols are used to form segmented products including Spandex that is used for clothing including undergarments and swimwear (Picture 5.11). These products are one basis for segmented elastomers where aromatic PUs that form hydrogen bonding act as the “hard” segment, and the polyols such as poly(ethylene glycol) (PEG) form the “soft” segment. These segmented PUs can be thermoplastics or thermosets depending on whether or not cross-linking is introduced.



PICTURE 5.10 Polyurethane-filled pillows and cushions.



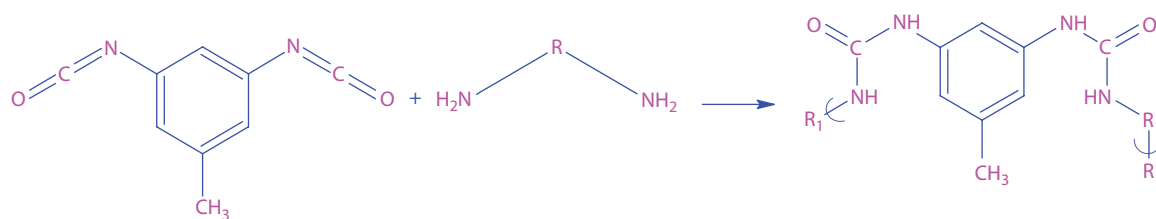
PICTURE 5.11 Swim wear made from a nylon/spandex blend.



RIM is increasing in importance and emphasizes the production of thermoset PUs. Here, liquid monomers are mixed together under high pressure prior to injection into the mold. Polymerization occurs within the mold. Most automotive dash panels are RIM-produced (Picture 5.12). Notice the tough surface and semiflexible underbelly of the dash. The amount of “foam” formation is controlled to give the finished product.

PUs are also widely used as coating materials sold as finished polymers, two-part systems, and prepolymer systems. Water-based PU systems are now available allowing easy home use. Aromatic diisocyanate-derived coatings generally offer poor external light stability, while aliphatic-derived systems offer good light stability.

Polyureas (Equation 5.67) are made similar to PUs, except diamines are employed in place of alcohols.



(5.67)



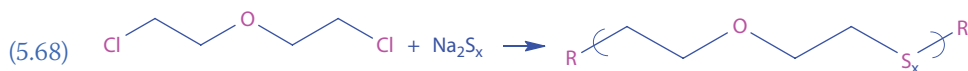
PICTURE 5.12 One-piece RIM-molded dashboard.

The diisocyanate can be aliphatic or aromatic and it can be a monomer, oligomer, or polymer where the amine links together the isocyanate functional groups. A number of polyureas are actually a resin blend that can contain amine-terminated polymers or amine-terminated chain extenders.

Polyureas are used where toughness is needed such as in truck bed liners. Truck bed liners can also be sprayed onto the bed surface. Bridges and pipes are increasingly being coated with polyureas since these last longer than simply painting these surfaces. Tanks, sewers, manholes, and roofs are often coated with polyureas. Railcars are increasingly being coated with polyureas for abrasion protection. In all of these applications, corrosion protection is essential and PUs offer good stability to weather and many chemicals. It is also finding application where water retention is needed such as in waste water treatment and landscape and water containment. It is being sprayed over foam creating architectural designs. Polyureas are used for flooring and parking decks because they can be rapidly applied and offer good protection when the floors are cleaned. Some automotive objects are formed from polyurea RIM systems replacing other molded pieces.

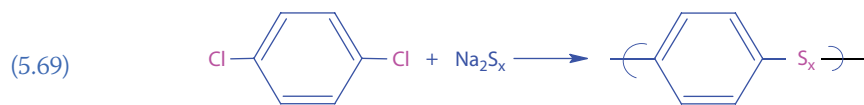
5.10 POLYSULFIDES

Thiokol (Equation 5.68), which was the first synthetic elastomer, was synthesized by Patrick in the 1920s, by the condensation of alkylene dichlorides and sodium polysulfides. These solvent-resistant elastomers have limited uses because of their foul odor. They can be reduced to liquid polymers that can be reoxidized to solid elastomers used in caulking material and some rocket propellant formulations.



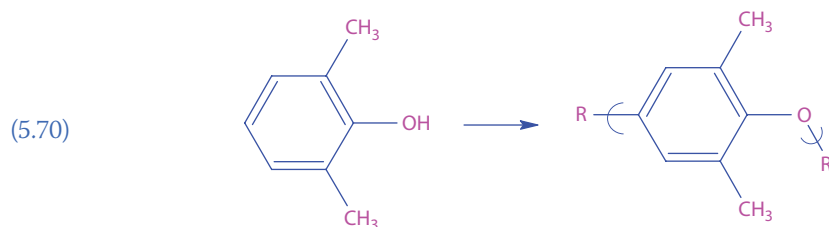
Because natural sulfur has eight sulfur atoms contained within each molecule, the number of sulfur atoms is generally variable being 1–8.

Poly(phenylene sulfide) (PPS; Ryton) is a solvent-resistant plastic that is useful in high-temperature service (Equation 5.69). PPS is used for pumps, sleeve bearing, cookware, quartz halogen lamp parts, and electrical appliance housings.



5.11 POLYETHERS

Hay, in 1956, discovered an oxidative coupling catalyst that allowed the production of polymeric aromatic ethers. The hope was to make polymers from readily available starting materials, mainly phenol. The main aromatic polyether today is derived not from phenol but rather from the catalytic coupling of 2,6-dimethylphenol. The resulting polymer is referred to as poly(phenylene ether) or poly(phenylene oxide) (PPO) (5.70). While called PPO, it is actually composed of phenylene oxide units containing methyl groups in the 2 and 6 positions of the phenylene moiety. PPO is made by a room temperature oxidation brought about by bubbling oxygen through a solution of the phenol in the presence of copper (I) chloride and pyridine. Initially, there was not a ready, inexpensive source of 2,6-dimethylphenol but because of early found positive properties of PPO, an inexpensive source of 2,6-dimethylphenol was found and both the monomer and polymer became commercial in 1964.

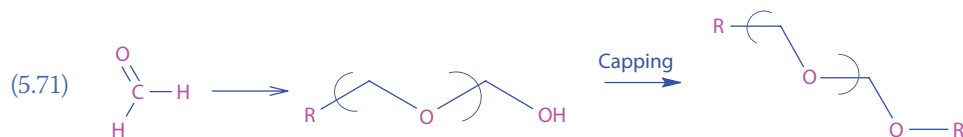


PPO has a very high T_g of 215°C and a T_m of about 270°C and exhibits good hydrolytic stability, but it has a very high melt viscosity and a tendency to oxidize and gel at processing temperatures. In spite of these negative processing features, PPO showed good compatibility with polystyrene and so has found a place in the marketplace.

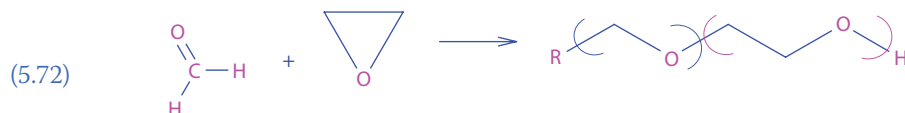
The Noryl trade name covers a variety of PPO-intensive materials, the most important being with polystyrene. While the methyl groups discouraged good interactions between PPO chains, the aromatic character positively interacts with the phenyl group on the polystyrene and the methyl groups interact positively with the aliphatic polystyrene backbone. Unlike most polymer mixtures, the combination of PPO and polystyrene forms a miscible blend. These blends and alloys with polystyrene raise the heat distortion temperature to over 100°C allowing production of materials that can be boiled. Combinations with PS, in particular high-impact polystyrene, are more easily processed and the PPO imparts needed flame resistance. The PS adds flexibility and lowers the melting point. The combinations also offer good hydrolytic stabilities and electrical properties, and they are relatively lightweight. Noryl is widely used in switch boxes because of its good electrical resistance. It can also be modified by addition to glass and other mineral fillers and is especially adaptable to metallizing. PPO-extruded sheet is being used for solar energy collectors, lifeguards on broadcasting towers, airline beverage cases, and window frames.

Aliphatic polyethers are also referred to as polyacetals. Polyoxymethylene (POM) precipitates spontaneously from uninhibited aqueous solutions of formaldehyde and was isolated by Butlerov in 1859. Staudinger, in the 1920s and 1930s, experimented with the polymerization of formaldehyde but failed to produce chains of sufficient length to be useful. While pure formaldehyde readily polymerized, it also spontaneously depolymerizes and unzippers. In 1947, DuPont began a program to make useful polymers from formaldehyde since formaldehyde is inexpensive and

readily available. After 12 years, they announced the commercialization of the polymer from formaldehyde, POM, under the trade name Delrin. The “secret” was capping the end groups by acetylation of the hydroxyl end groups, thus preventing the ready unzipping of the polymer chain (Equation 5.71). POM has a T_g of -75°C and a T_m of 180°C .



Celanese came out a year later with a similar product under the trademark Celcon. Celanese circumvented DuPont's patent on the basis of employing a copolymer variation that allowed enhanced stabilization against thermal depolymerization (Equation 5.72). The copolymer has a T_m of 170°C .



POMs are also employed in plumbing and irrigation because they resist scale accumulation and have good thread strength, torque retention, and creep resistance. POMs have been employed to assist in the flow of water in fire hoses, water displays, and supposedly for some large ships it is “squirted” from the front of the ship to cut down on friction because they help align the water allowing an increased fuel efficiency.

Commercially, the most important polyether is known as poly(ethylene glycol) (PEG), which is also known as poly(ethylene oxide) (PEO) or polyoxyethylene (POE). While these names are synonymous, historically, PEG was used for lower chained products, PEO for longer chains, and POE for both. Here we will simply use the term PEG. PEG comes in a variety of chain length from low that are liquids to high that are solids.

PEG is generally synthesized from the ROP of poly(ethylene oxide) in water (5.73). Mixtures of water, ethylene glycol and ethylene glycol oligomers, are often used.

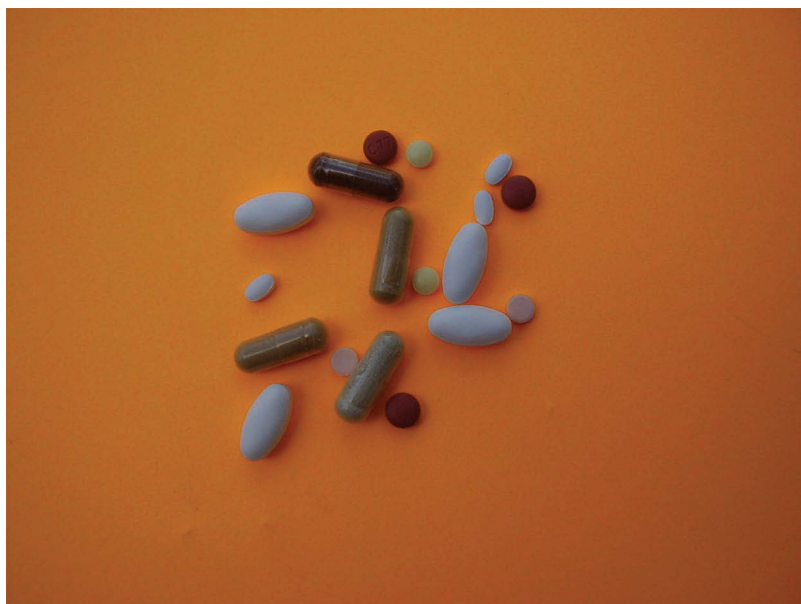


PEGs are generally designated as to some average molecular weight. Thus, PEG4000 corresponds to $n \approx 90$ (that is $4000/44 \text{ amu/unit}$).

PEGs come with a variety of end groups. Thus, the monofunctional methyl ether of PEG, methoxypoly(ethylene glycol) has one of the end groups a methoxy rather than the usual hydroxyl. They also come in a variety of geometries. Star PEGs have 10–100 PEG units radiating from a central core. Branched PEGs have 3–10 PEG chains radiating from a central core. Comb PEGs have multiple PEG chains grafted to a polymer backbone.

PEGs have a low toxicity and are employed in a number of products. It forms the basis for a number of laxatives such as MiraLax, GlycoLax, and Movicol. It is used in a number of sexual lubricants and skin creams. Bowel irrigations often employ PEG generally with some electrolytes to be used before surgery, colonoscopy, or in drug overdoses. It is sold under such trade names as Colyte, TriLyte, Fortrans, GoLately, and GlycoLax. It is attached to selected protein drugs to allow a longer acting medicinal effect. PEG-interferon alpha is used to treat hepatitis C and PEG-filgrastim is used to treat neutropenia. It is also employed as a coating for many pills to allow the medication to pass through the area before it is exposed to the harsh stomach environment (Picture 5.13). Some coatings are designed to help protect the medication through the stomach area.

It is employed as the soft segment in PUs. PEG is used in toothpaste as a dispersant and as a lubricant in eye drops. It is also being used in certain body armor. Dr. Pepper adds PEG as



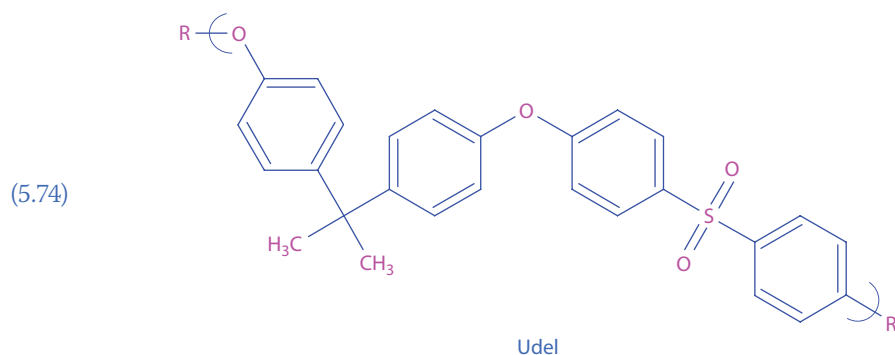
PICTURE 5.13 Pills coated with PEG.

an antifoaming agent. It has been used to help preserve wood replacing water giving the wood increasing dimensional stability. Certain gene therapy vectors such as viruses can be coated with PEG to protect them from inactivation by immune systems and to detarget them from organs where they could build up causing a toxic effect.

Because of their ready water solubility, PEGs are often used to impart water solubility to a polymer. This approach has been used to make electrically conductive polymers water soluble as well as a number of drugs water soluble.

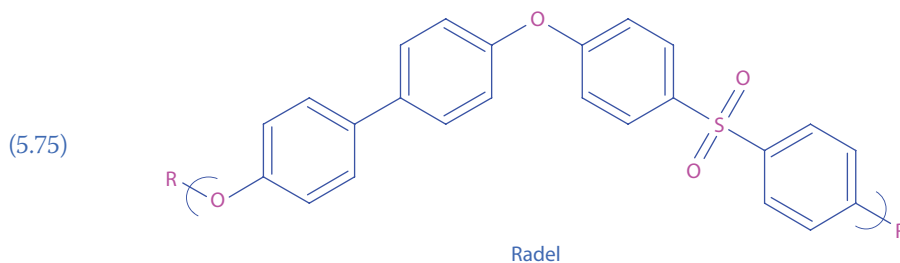
5.12 POLYSULFONES

Polysulfones exhibit excellent thermal oxidative resistance, and resistance to hydrolysis and other industrial solvents, and creep. The initial commercial polysulfones were synthesized by the nucleophilic replacement of the chloride on bis(*p*-chlorophenyl) sulfone by the anhydrous sodium salt of BPA. It became commercially available in 1966 under the trade name Udel (5.74). It exhibits a reasonably high T_g of 190°C.



Union Carbide, in 1976, made available a second generation polysulfone under the trade name Radel. Radel (5.75) was formed from the reaction of a bisphenol and bis(*p*-chlorophenyl) sulfone.

This polysulfone exhibits greater chemical/solvent resistance, a greater T_g of 220°C, greater oxidative stability, and good toughness in comparison to Udel.



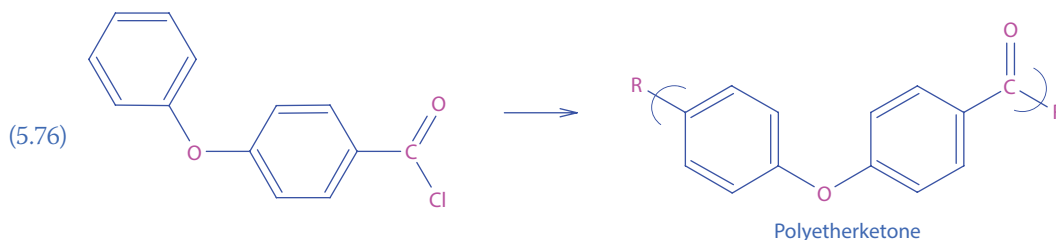
Polysulfones can also be made from the Friedel–Crafts condensation of sulfonyl chlorides.

Polysulfones are used for ignition components, hair dryers, cookware, dielectric in capacitors, and structural foams. Because of their good hydrolytic stability, good mechanical properties, and high thermal endurance, they are good candidate materials for hot water and food handling equipment, alkaline battery cases, surgical and laboratory equipment, life support parts, autoclavable trays, tissue culture bottles, surgical hollow shapes, and film for hot transparencies. Membranes for use in hemodialysis, gas separation, food and beverage processing, and waste water recovery have also been produced from polysulfones. Their low flammability and smoke production, because of their tendency for polycyclic formation on thermolysis and presence of moieties that are already partially oxidized, makes them useful as materials for the aircraft and automotive industries.

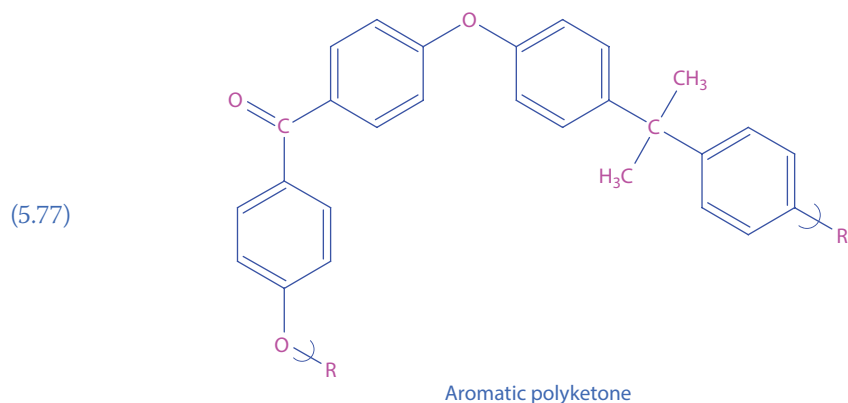
5.13 POLY(ETHER ETHER KETONE) AND POLYKETONES

Aromatic polyketones are semicrystalline materials that contain both ketone groups generally flanked by aromatic units. Many also have included within them ether moieties that allow for some flexibility and better processing. They have good thermal stabilities, as well as offering good mechanical properties, flame resistance, impact resistance, and resistance to the environment.

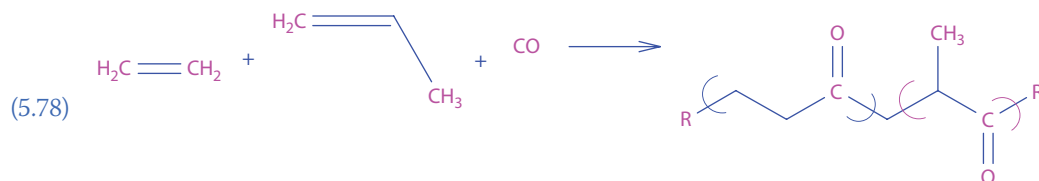
Polyetherketone was introduced by Raychem in the 1970s (Equation 5.76). It is made by the Friedel–Crafts reaction requiring good solvents or an excess of aluminum chloride to keep the polymer in solution allowing polymer growth to occur. Most polymerizations require that the reactants remain mobile, through solution or being melted, so that the individual units involved in the reaction can get together. Rapid precipitation of growing polymer chains often results in the formation of only oligomeric to small chains.



ICI has introduced a new crystalline poly(ether ether ketone) (5.77). Applications include compressor plates, valve seats, thrust washers, bearing cages, and pump impellers. In the aerospace industry, they are employed as aircraft fairings, fuel valves, and ducting. They are also used in the electrical industry as wire coating and semiconductor wafer carriers.

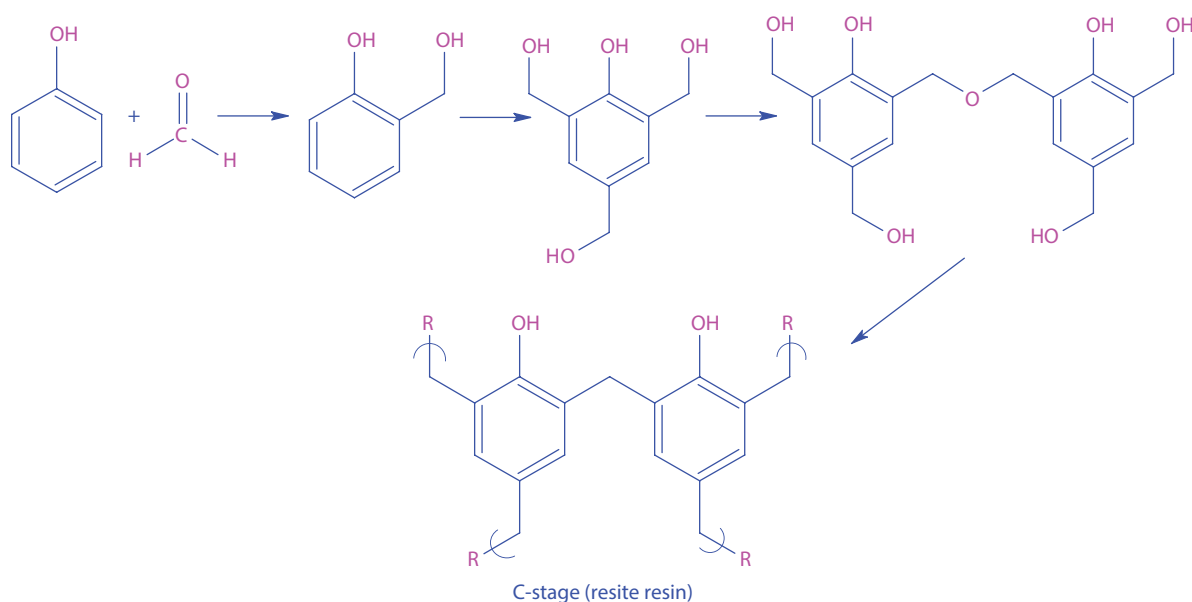


Aliphatic polyketones are made from the reaction of olefin monomers and carbon monoxide using a variety of catalysts. Shell commercialized a terpolymer of carbon monoxide, ethylene, and a small amount of propylene in 1996 under the trade name Carilon (Equation 5.78). They have a useful range between the T_g (15°C) and T_m (200°C) that corresponds to the general useful range for most industrial applications. The presence of polar groups causes the materials to be tough with the starting materials readily available.

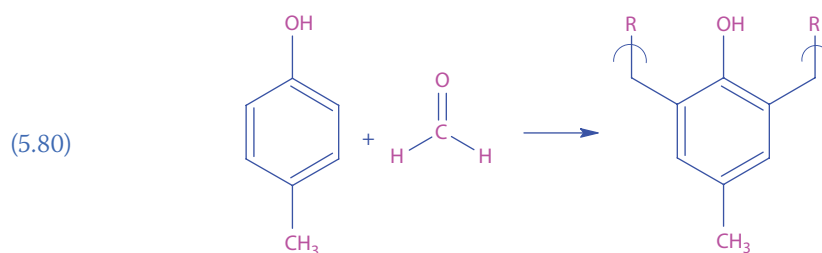


5.14 PHENOLIC AND AMINO PLASTICS

Baekeland found that a relatively stable resole prepolymer could be obtained by the controlled condensation of phenol and formaldehyde under alkaline conditions. These linear polymers (PF) may be converted to infusible cross-linked polymers called resites by heating or by the addition of mineral acids. As shown in Equation 5.79, the initial products produced when formaldehyde is condensed with phenol are hydroxybenzyl alcohols. The linear resole polymer is called an A-stage resin, and the cross-linked resite is called a C-stage resin.



Baekeland recognized that the trifunctional phenol would produce network polymers and thus used difunctional ortho- or para-substituted phenols to produce linear paint resins. Linear thermoplastic products are formed by alkaline or acid condensation of formaldehyde with phenol derivatives such as *p*-cresol (Equation 5.80).



Since the acid condensation of 1 mol of phenol with 1.5 mol of formaldehyde produced thermoset C-stage products, Baekeland reduced the relative amount of formaldehyde used and made useful novolac resins in a two-step process. Thus, stable A-stage novolac resin is produced by heating 1 mol of phenol with 0.8 mol of formaldehyde in the presence of acid. After removal of water by vacuum distillation, the A-stage resin produced is cooled and then pulverized. The additional formaldehyde required to convert this linear polymer into a thermoset resin is supplied by hexamethylenetetramine. The latter, which is admixed with the pulverized A-stage resin, is produced by the condensation of formaldehyde and ammonia. Other ingredients such as filler, pigments, and lubricants are mixed with the resin and hexamethylenetetramine. The A-stage resin is further polymerized. The term phenol molding compound is applied to the granulated B-stage novolac resin.

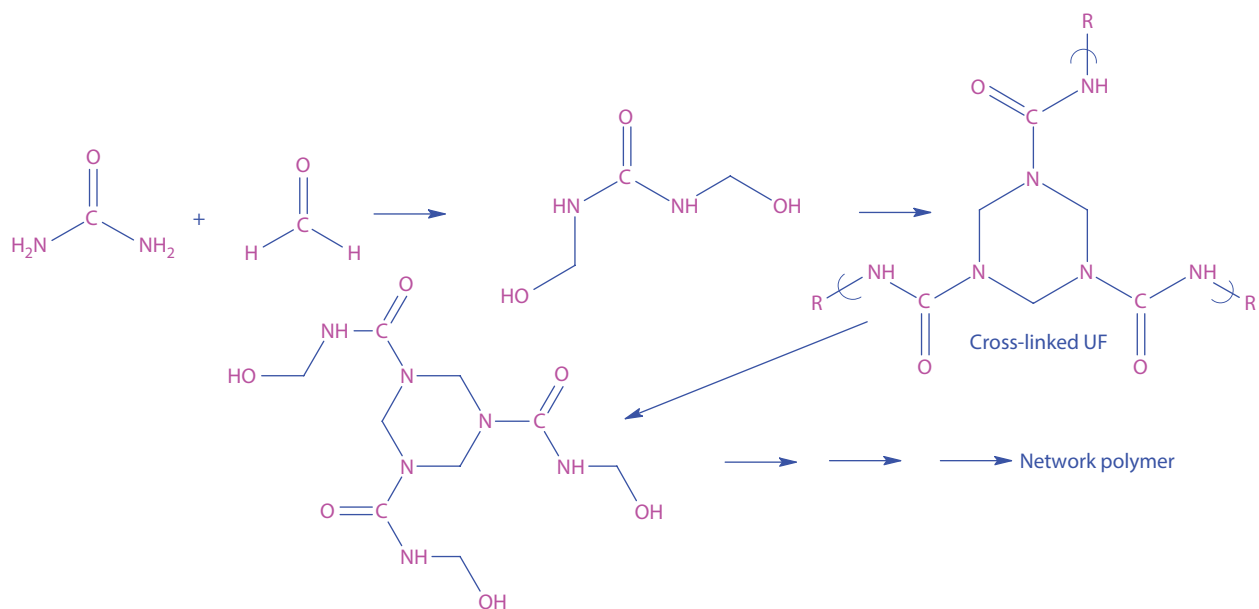
While the condensation of urea and formaldehyde was described in 1884, urea-formaldehyde (UF) resins were not patented until 1918. Comparable products, based on the condensation of formaldehyde and melamine (2,4,6-triamino-1,3,5-triazine), were not patented until 1939. The term melamine-formaldehyde (MF; Equations 5.81 and 5.82) is used to describe these products.

Plywood is widely used in the building industry. The individual sheets of wood are weak but when fitted together using a polymeric glue are strong. The plies or layers of woods are generally arranged at right angles to one another resulting in increased strength (Picture 5.14). Indoor plywood is typically bound together using less expensive UF adhesive that has relatively limited

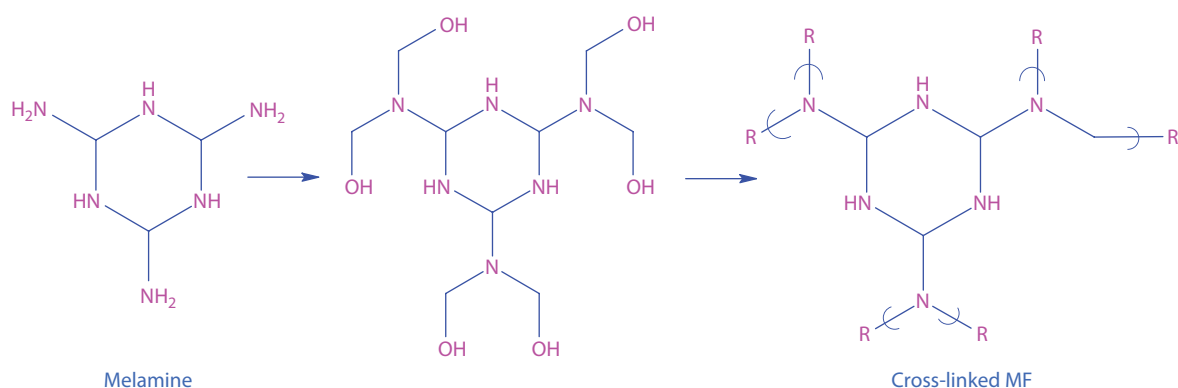


PICTURE 5.14 Plywood showing varying layers laid at a right angle to one another.

water resistance. Plywood that is to be used outdoors and marine-grade plywood use more expensive phenol-formaldehyde as the adhesive. This gives the plywood greater ability to resist delamination brought about through exposure to water.



(5.81)



(5.82)

Urea and melamine are tetra- and hexafunctional molecules. However, the formation of a network polymer is prevented by adding alcohols such as *n*-butanol and by condensing with formaldehyde at low temperatures under basic conditions. While phenol resins have better moisture and weather resistance than urea resins, the latter are preferred for light-colored objects. For example, the interior layers of laminated countertops are bonded together by phenolic resins, but either urea or melamine resins are used for the decorative surface. Melamine plastics are more resistant to heat and moisture than UF and thus are preferred for decorative surfaces and for dinnerware (Picture 5.15).

5.15 SYNTHETIC ROUTES

The previous sections describe the synthesis of a number of important condensation polymers. Here, we will briefly consider the three main synthetic techniques utilized in the synthesis of these polymers.



PICTURE 5.15 Melamine dinnerware.

The *melt technique* is also called other names to describe the same or similar processes. These names include high melt, bulk melt, and simply bulk or neat. The melt process is an equilibrium-controlled process in which polymer is formed by driving the reaction toward completion, usually by removal of the by-product. For polyesterifications involving the formation of hydrogen chloride or water, the driving force is the removal of the hydrogen chloride or water. Reactants are introduced along with any added catalyst to the reaction vessel. Heat is applied to melt the reactants allowing them to condense together. The heat is maintained or increased above this melt temperature. Pressure is reduced to remove the condensate. Typical melt polymerizations take several hours to several days before the desired polymer is produced. Yields are necessarily high.

Solution condensations are also equilibrium processes, with the reaction often driven by removal of the by-product by distillation or by salt formation or precipitation. Many solution condensations are run near room temperature. Solvent entrapment is a problem, but since a reaction may occur under considerably reduced temperatures, compared to the melt process, thermally induced side reactions are minimized. Side reactions with the solvent may be a problem. Because the reactants must be energetic, many condensations are not suitable for the solution technique.

The *interfacial technique* (IF), while old, gained popularity with the work of Morgan and Carraher in the 1960s and 1970s. Many of the reactions can be carried out under essentially nonequilibrium conditions. The technique is heterophasic, with two fast-reacting reactants dissolved in a pair of immiscible liquids, one of which is usually water. The aqueous phase typically contains the Lewis base such as diol, diamine, or dithiol. The organic phase contains the Lewis acid, generally an acid halide, dissolved in a suitable organic solvent such as hexane. Reaction occurs near the interface, hence the name. With all the potential that the interfacial system offers, it has not attracted wide industrial use because of the high cost of the necessarily reactive monomers and cost of solvent removal. One commercial use for the IF system is the production of polycarbonates. Another involves the synthesis of aramids. Morgan and others noted that some polymers formed with rapid stirring would remain in solution for awhile before they precipitated. The problem with aramids was the need to form fibers from their solutions. Thus, the aromatic nylons had to be redissolved after formation. Today, aramids are synthesized using rapidly stirred systems where the polymer solution is sent through a small hole into a nonsolvent. This allows fibers to be produced without needing to redissolve the polymer.

Table 5.3 contains a comparison of these three major polycondensation processes.

TABLE 5.3 Comparison of Requirements for Different Polycondensation Techniques

Requirement	Melt	Solution	Interfacial
Temperature	High	Limited only by the MP and BP of the solvent used	Generally about room temperature
Stability to heat	Necessary	Unnecessary	Unnecessary
Kinetics	Equilibrium, stepwise	Equilibrium, stepwise	Generally nonequilibrium, chain-wise
Reaction time	1 hour to several days	Several minutes to 1 hour	Several seconds to 1 hour
Yield	Necessarily high	Less necessary high	Low to high
Stoichiometric equivalence	Necessarily high	Less necessary high	Less necessary
Purity of reactants	Necessary	Less necessary	Less necessary
Equipment	Specialized, often sealed	Simple, open	Simple to complex, can be open
Pressure	High, low	Atmospheric	Atmospheric

5.16 LIQUID CRYSTALS

Every day of our lives, we “run across” liquid crystals, LCs. They are commonly found in computer monitors, digital clocks and other “readout” devices, etc.

Reintzer, in 1888, first reported “liquid crystal” behavior. In working with cholesteryl esters, he observed that the esters formed opaque liquids, which on heating turned clear. We now know, as a general rule, that many materials are clear if they are anisotropic and random or if the materials are composed of ordered molecules or segments of molecules, whereas they are opaque if there exists a mixture of ordered and disordered regions. Lehmann interpreted this behavior as evidence of a “third” phase that exists “between” the solid and isotropic liquid states. This new phase was named by Lehmann as the LC phase. Friedel called this phase the mesophase after the Greek word “mesos” meaning intermediate. The initial molecules investigated as LCs were large monomeric molecules.

Flory, in 1956, predicted that solutions of rodlike polymers could also exhibit LC behavior. The initial synthetic polymers found to exhibit LC behavior were concentrated solutions of poly(γ -benzyl glutamate) and poly(γ -methyl glutamate). These polymers exist in a helical form that can be oriented in one direction into “ordered groupings” giving materials with anisotropic properties.

LCs are materials that undergo physical reorganization where at least one of the rearranged structures involves molecular alignment along a preferred direction causing the material to exhibit nonisotropic behavior and associated birefringent properties, that is, molecular asymmetry.

Liquid crystalline materials can be divided into two large groupings—thermotropic and lyotropic. Thermotropic LCs are formed when “pure” molecules such as cholesteryl form ordered structures upon heating. When LCs occur through mixing with solvents, they are called lyotropic LCs.

Thermotropic LCs can be further divided into (a) enantiotropic materials where the LC phases are formed on both heating and cooling cycles and (b) mesotropic materials where the LCs are stable only on supercooling from the isotropic melt. The mesotropic LCs have been further divided into three groupings as follows:

- Smectic meaning “soap”
- Nematic meaning “thread”
- Cholesteric derived from molecules with a chiral center

LC polymers are typically composed of materials that are rigid and rodlike with a high length to breadth ratio or materials that have a disc shape. The smaller groupings that give the material LC behavior are called “mesogens.” These mesogens are simply portions of the overall polymer that are responsible for forming the anisotropic LC and that, in fact, form the LC segments.

Such mesogens can be composed of only segments from the backbone of the polymer, segments from the side chain or segments from both the backbone and side chain.

Mesogens form the ordered structures necessary to give the overall material anisotropic behavior. There have been identified a number of different mesogens groupings. Chains arranged so that the mesogen portions are aligned in one preferred direction with the ordering occurring in a 3D layered fashion compose one group of arrangements called smectic arrangements. Here, the lateral forces between the mesogen portions are relatively higher than the lateral forces between the nonmesogen portions allowing a combination of segments that permit “flowing” (the passage of nonmesogen portions) and segments that retain contact (mesogen portions) as the material flows imparting a “memory”-type behavior of the material. A number of different “packings” of the mesogens have been identified. The most ordered of the mesogenic groupings is called “smectic B,” which is a hexagonally, close-packed structure present in a 3D arrangement. A much less ordered grouping is called the “smectic A” phase. Here, there is a somewhat random distribution of the mesogens between the layers.

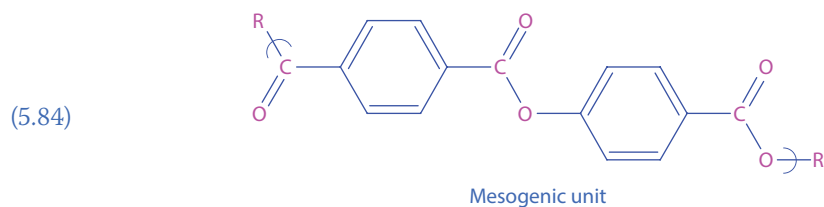
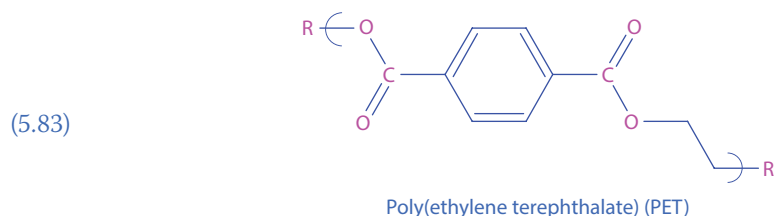
Nematic LCs offer much less order in comparison to smectic arrangements. Here, the directional ordering of the mesogen portions along one axis is retained, but the centers of gravity of the mesogen portions are no longer “coupled.” Thus, the forces between the chains are less resulting in a generally greater fluidity for nematic LCs in comparison with smectic structures. Nematic LCs also offer nonlinear behavior.

The chiral nematic assembly is formed by materials that have chiral centers and that form a nematic phase. Here, a “chiral-imposed twist” is imparted to the linear chains composing each layer resulting in a 3D helical arrangement.

The molecular asymmetry typically occurs not because of intermolecular interaction, but because two molecules cannot occupy the same space at the same time. Molecular chains can exist in a random arrangement until a given concentration is exceeded causing the molecules to rearrange in a more ordered fashion to accommodate the larger number of molecules within the same volume. Often, this occurs such that there is an ordered phase and a more random phase. As the concentration of polymer increases, the ordered phase becomes larger at the expense of the disordered phase. This increase in polymer concentration can occur via several routes such as addition of more polymer, addition of a solution containing a higher concentration of polymer, and evaporation of the solvent.

For crystalline polymer systems, transition from the crystalline structure to a mesophase structure occurs, whereas from amorphous polymer systems, the mesophase occurs after the T_g has occurred. Some polymer LC systems form several mesophases. Mesophases can be detected using DSC, x-ray diffraction, and polarizing microscopy.

Introduction of flexible “spacer” units such as methylene, methylene oxide, and dimethylsiloxane groups lowers the melting point and increase the temperature range within which the mesophase is stable. Often, these spacer units are introduced by copolymerization. Thus, pre-formed *p*-acetoxybenzoic acid is reacted with PET (5.83), introducing a mesogenic unit (5.84) in a polymer that has flexible spacer units (from the ethylene glycol) in it.



Along with the mesogen units contained within the polymer backbone, the mesogen units can occur as side chains. These mesogen units can be introduced either through reaction with monomers that contain the mesogen unit or through introduction with already formed polymers.

LC materials have also been employed as films, plastics, and resins. Poly(1,4-benzoate) has been marketed under the name Ekonol. It decomposes before it melts; hence it does not form LC melts. Copolymerization with 4,4'-biphenol and terephthalic acid gives Ekkcel. Ekkcel does melt before it decomposes. Certain forms can be compression molded and others injection molded. Reaction of poly(1,4-benzoate) with PET gives a material that can be injection molded. These LCs are chemical resistant, with high tensile strength. LC films with mesogenic side chains can be used in information storage devices.

5.17 MICROFIBERS

Microfibers are not a new chemically distinct fiber, but rather the term refers to fibers that have smaller diameters. DuPont first introduced microfibers in 1989. Microfibers have diameters that are less than typical fibers. Microfibers are half the diameter of fine silk fiber, one-quarter the diameter of fine wool, and 100 times finer than human hair. Denier, the weight in grams of 9000 m length of a fiber, is the term used to define the diameter or fineness of a fiber. While the definition for the thickness of microfibers is varied, a typical definition is that microfibers have a denier that is 0.9 denier or less. For comparison, the nylon stocking is knit from 10 to 15 denier fiber.

Microfibers allow a fabric to be woven that is lightweight and strong (Picture 5.16). Microfibers can be tightly woven so that wind, rain, and cold do not easily penetrate. Rainwear manufacturers use microfibers for this reason. They also have the ability to allow perspiration to pass through them. Thus, so-called microfiber athletic wear is becoming more commonplace. Microfibers are also very flexible because the small fibers can easily slide back and forth on one another. The first fabric made from microfiber was Ultrasuede™ where short polyester microfibers were imbedded into a PU base. Today, microfibers are made mainly from polyesters, nylon, acrylic, and rayon fibers.

The use of the term microfibers is now extended to glass and Teflon-related materials. Here we will restrict ourselves to only fabric applications.



PICTURE 5.16 Microfiber blankets and throws.

In 1970, Toray Industries scientist Miyoshi Okamoto created the first microfiber. A few months later, his colleague Toyohiko Hikota developed a process that allowed the production of fabric that was later trademarked as Ultrasuede. Ultrasuede was produced from PET polyester fibers so thin that a pound of them laid end-to-end would reach from the earth to the moon and back. Ultrasuede is soft and supple, resistant to stains and discoloration, and machine washable and dry cleanable.

Because of progress made in spinning and fiber processing, smaller fibers can be routinely made with varying configurations, coatings, etc. Microfiber production is mainly achieved using three techniques. The first technique will be illustrated using the processing technique employed to manufacture Ultrasuede.

The processing to form Ultrasuede is complex. First, ultra-microfibers are spun that are so light and fine that a single 50 miles long strand would weigh less than 1 g. These ultra-microfibers are then extruded through spinnerets creating a configuration that is similar to that present in tendons and hair bundles. These strands are then transformed by ironing, curling, cutting, and needle punching into a feltlike material that is then impregnated with a special adhesive binder. The material is then formed into the desired contours and the protective coating is dissolved with a solvent and the material undergoes further processing creating the nonwoven fabric.

Microfibers are also made by simple extrusion through a spinneret with a smaller hole than normally employed for fiber production. The third method involves spinning a bicomponent fiber and using a solution to split the fiber into smaller pieces. Initially, bicomponent fibers in the range of 2–4 denier are spun after which the fibers are split into microfibers. If a 32-segment pie of nylon/polyester fiber is used, the final denier is in the range of 0.1 denier. Brushing and other techniques can be used to enhance the effects. Splittable, hollow fibers are also being used to achieve fiber splitting. For instance, for polyester/polypropylene fiber combinations, “natural” splitting occurs after passage through the spinneret. After mechanical drawing, the yarn has a denier of about 0.2 well within that described for microfibers. More recently, tipped fibers are being studied. Here, a bicomponent fiber is made except the second polymer is placed on the tip of the fiber. After spinning, the fibers are twisted and then wet heat is applied resulting in the tips of the fibers breaking apart into microfibers with a denier of about 0.2. Because the two different polymers have different heats of elongation, coefficients of expansion, etc., the physical changes cause the two polymer components to break apart when heated.

The shape of the microfiber influences the end properties. For instance, Tomen has developed Technofine™ that is a polyester microfiber with a “W” shape cross section. The increased surface allows a more rapid transport of water away from the skin and also increases the evaporation rate making garments made from it quicker drying and more adsorbent.

Most textiles have limited elongation but many of the microfiber textiles have elongations of 100%.

Currently, no industry regulations exist that describe the amount of microfiber that must be present to call it a microfiber material. Even so, typically industrial use calls for a material to be at least 35%–40% microfiber to be called a microfiber product. Microfibers are most commonly used in dress and blouse garments. They are also used to make hosiery, ties, scarves, intimate apparel, curtains, draperies, sheets, towels, rainwear, swimwear, blankets, tents, sleeping bags, track and jogging wear, and many other items. The greater surface area results in a fabric with deeper, richer, and brighter colors possible.

The care of microfiber products is similar to that of the normal-fiber materials made from the same polymer. One caution is heat sensitivity. Because the fibers are so fine, heat penetrates more quickly causing them to scorch or glaze more quickly than “normal” fibers if too much heat is applied or heat is applied over too long a period. Typically, microfibers are wrinkle resistant, but if ironing is done, then it should be accomplished using lower temperatures and only as directed.

SUMMARY

1. Many naturally occurring and some synthetic polymers are produced by condensation reactions many of which are described kinetically by the term stepwise polymerization. A high fractional conversion is required to form linear polymers such as polyesters,

nylons, polysulfides, PUs, polycarbonates, polysulfones, polyimides, PBIs, and polyethers. But a high fractional conversion is not required for the production of network, cross-linked, products such as epoxy, phenol, urea, formaldehyde, and melamine resins. One major exception to the production of condensation polymers through the stepwise kinetic process is the use of the interfacial reaction system employing reactive reactants that follows a chain-wise kinetic process. The interfacial system is employed to produce polycarbonates and some aramids. The remainder of the condensation polymers are generally produced using the melt and solution techniques.

2. The rate expressions and values, mechanisms, and the activation energies for the condensation reactions forming polymers are similar to those of small molecule reactions. Reaction rate increases with temperature in accordance with the Arrhenius equation. Average DP also increases as the reaction temperature increases to the ceiling temperature where polymer degradation occurs. Long chains are only formed at the conclusion of classical polycondensation processes.
3. The average \overline{DP}_n for formation of linear condensation polymers can be calculated using the Carothers' equation, $\overline{DP}_n = 1/(1 - p)$.
4. Cross-linked products are formed when the functionality of either reactant is greater than two. Linear products are formed when the functionality of both reactants is two.
5. Condensation polymers tend to exist below their T_g at room temperature. They typically form fairly ordered structures with lots of strong interactions between the various chains giving strong materials with some, but not much, elongation when stretched. They are normally used as fibers and plastics. They have high stress-strain ratios.

GLOSSARY

Alkyds: Term originally used to describe oil-modified polyester, but now used for many polyester plastics and coatings.

Allophanates: Reaction product of a urethane and an isocyanate.

Amino resins: Urea and melamine-formaldehyde resins.

Aramids: Aromatic polyamides.

A-stage: Linear prepolymer of phenol and formaldehyde.

Bakelite: Polymer produced by Leo Baekeland by condensation of phenol and formaldehyde first by Leo Baekeland.

Bifunctional: Molecule with two active functional groups.

Bisphenol A: 2,2'-Bis(4-hydroxyphenyl)propane.

B-stage: Advanced A-stage resin.

Carbamate: A urethane.

Carbamic acids: Unstable compounds that decompose spontaneously giving amines and carbon dioxide.

Carothers, W.H.: Inventor of nylon who also standardized much of the polymer nomenclature we use today.

Carothers equation: $\overline{DP}_n = 1/(1 - p)$.

Condensation reaction: Reaction in which two molecules react producing a third molecule and a by-product such as water.

Cyclization: Ring formation.

Dacron: Trade name for PET fiber.

Drying: Cross-linking of an unsaturated polymer generally in the presence of oxygen.

Drying oil: An unsaturated oil like tung oil.

Engineering plastic: Plastics whose physical properties are good enough to permit their use as structural materials; generally, they can be cut, sawn, and drilled.

Epoxy resin: Polymer produced by the condensation of epichlorohydrin and a dihydric alcohol or by the epoxidation of an unsaturated molecule.

Ester interchange: Reaction between an ester of a volatile alcohol and a less volatile alcohol in which the lower boiling alcohol is removed by distillation.

- Filament:** Extrudate when a polymer melts or solution is forced through a hole in a spinneret.
- Functionality:** Number of active functional groups present in a molecule.
- Functionality factor:** Average number of functional groups present per reactive molecule in a mixture of reactants.
- Furan resin:** Resin produced from furfuryl alcohol or furfural.
- Gel point:** Point at which cross-linking begins to produce polymer insolubility.
- Glyptals:** Polyesters, usually cross-linked by heating.
- Incipient gelation:** Point where the DP reaches infinity.
- Interfacial polymerization:** One in which the polymerization reaction occurs near the interface of two immiscible liquids.
- Kodel:** Trade name for a PET fiber.
- Ladder polymer:** Double-chained temperature-resistant polymer.
- Laminate:** Layers of sheets or paper or wood or other material adhered by resins and pressed together like plywood.
- Long oil alkyd:** One obtained in the presence of 65%–80% of an unsaturated oil.
- Medium oil alkyd:** Alkyd obtained in the presence of 50%–65% of an unsaturated oil.
- Melamine-formaldehyde resin:** Resin produced by the condensation of melamine and formaldehyde.
- Molding compound:** Name given to describe a mixture of a resin and essential additives.
- Nonoil alkyd:** An oil-free alkyd containing no unsaturated oils.
- Novolac:** Polymers prepared by the condensation of phenol and formaldehyde under acidic conditions.
- Nylon:** Synthetic polyamide.
- Oil length:** Term used to indicate the relative percentage of unsaturated oils used in the production of alkyds.
- Phenoxy resin:** Polymer with hydroxyl pendent groups resembling an epoxy resin without epoxy groups.
- Poly(ethylene terephthalate) (PET):** Linear polyester used to produce fibers and for blow-molding preparation of soft drink bottles; produced from terephthalic acid and its esters and ethylene glycol.
- Prepolymer:** Low-molecular-weight material (oligomer) capable of further polymerization.
- Resite:** Cross-linked resole.
- Resole:** Linear polymer prepared by condensation of phenol and formaldehyde under alkaline conditions.
- Schotten–Baumann reaction:** Traditionally the reaction between an acid chloride and a Lewis base.
- Short oil alkyd:** An alkyd obtained in the presence of 30%–50% of an unsaturated oil.
- Step-reaction polymerization:** Polymerization in which polyfunctional reactants react to produce larger units in a continuous stepwise manner.
- Thiokol:** Trade name for a polysulfide elastomer.
- Unsaturated polyester:** Term used to describe alkyds with unsaturated chains, particularly those produced by the condensation of maleic anhydride and ethylene glycol.
- Urea-formaldehyde resin:** Resin produced by condensation of urea and formaldehyde.
- Wasted loops:** Formation of cyclic compounds instead of polymer chains.

EXERCISES

1. Which of the following will give a polymer when condensed with adipic acid: (a) ethanol, (b) ethylene glycol, (c) glycerol, (d) aniline, or (e) ethylenediamine?
2. Could Carothers have produced strong polyester fibers by ester interchange or Schotten–Baumann reactions using aliphatic reactants?
3. Which would be useful as a fiber: (a) poly(ethylene terephthalate) or (b) poly(hexamethylene terephthalate)?
4. If the fractional conversion in an ester interchange reaction is 0.99999, what would be the average degree of polymerization of the polyester produced?

5. Use the logarithmic form of the Arrhenius equation to show that the value of the rate constant k increases as the temperature increases.
6. What is the first product produced when a molecule of sebacoyl chloride reacts with a molecule of ethylene glycol?
7. What is the next product formed in Question 6?
8. How would you improve the strength of the filament produced in the nylon rope trick without changing the reactants?
9. Name the product produced by the condensation of adipic acid and 1,4-tetramethylenediamine?
10. In which reaction would you expect the more “wasted loop”: the reaction of oxalyl chloride with (a) ethylenediamine or (b) 1,6-hexanediamine?
11. Which system would be more apt to produce “wasted loops”: (a) a dilute solution or (b) a concentrated solution?
12. If the values of A_0 and k are 10 mol/L and 10^{-3} L mol/s, respectively, how long would it take to obtain an average DP of 37?
13. Which will give the lower index of polydispersity: (a) $p = 0.000$ or (b) $p = 0.90$?
14. If you used a 2% molar excess of bisphenol A with TDI, what would be the maximum average degree of polymerization obtainable assuming $p = 1$?
15. Why would you predict the product obtained in Question 14 be a useful fiber assuming an average DP of 100?
16. Name the product formed from the reaction of a phenol with formaldehyde.
17. Give the Carothers equation. What is its significance?
18. What is the product of polymerized formaldehyde? Is it stable?
19. What is the product of a diol and diisocyanate? What are general uses of this product?
20. Which would be the better or stronger fiber: one made from an ester of (a) terephthalic acid or (b) phthalic acid?
21. What would be the deficiency of a nylon film that was stretched in one direction only?
22. Which would be more flexible: (a) poly(butylene terephthalate) or (b) poly(hexamethylene terephthalate)?
23. Which would be more apt to deteriorate in the presence of moisture: (a) Lexan molding powder or (b) Lexan sheet?
24. What reactants are typically employed to make a polycarbonate?
25. How would you prepare a nylon with greater moisture resistance than nylon 66?
26. How would you prepare a nylon that would be less “clammy” when used as clothing?
27. Which would be higher melting: (a) a polyamine or (b) a polyester with similar members of methylene groups in the repeat unit?
28. Why is a methoxymethylated nylon more flexible than nylon?
29. Why is Bakelite not used in forming molded objects?
30. Isn't it wasteful to decompose a diisocyanate by hydrolysis to produce foams?
31. How would you prepare a hydroxyl-terminated polyester?
32. For the acid-catalyzed condensation of ethylene glycol with terephthalic acid, what is the relationship between DP and extent of reaction?
33. For stepwise kinetics, what happens to chain length as time increases?
34. Why do polyurethanes and epoxy resins have good adhesive properties?
35. Why are furan resins relatively inexpensive?
36. To produce cross-linked polyesters, what is normally present?
37. Could you produce a soluble novolac resin from resorcinol?
38. Can you explain why there are so many terms used, such as novolac and resole, in phenolic resin technology?
39. Why isn't Bakelite used for dinnerware?
40. Which of the following could be a non-petrochemical plastic: (a) Bakelite, (b) urea plastics, or (c) melamine plastics?
41. Which would produce the better fiber: the reaction product of phthalic acid and (a) 1,4-butanediol or (b) 2-hydroxybutanal?
42. Why is PEG widely used in drug delivery?
43. What are aramids?
44. What are general properties of aramids?

45. As noted in the text, there is an interesting problem occurring with PET recycling. Some manufacturers are including additives intended to help in the degradation of PET. However, the presence of these additives limit the number of times that PET can be recycled. What might be done to help solve this problem?

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Ionic Chain Reaction and Complex Coordination Polymerization (Addition Polymerization)

In the following three chapters, we will examine, in comparison to condensation polymers, polymers that have low seconding bonding between polymer chains. The presence of these low-energy bonding forces allows for less energy being required for elongation. Many of these polymers have glass transition temperatures below room temperatures allowing relatively easy *sliding* of chains past one another resulting in a flexible material. Many of these materials are employed in the production of elastomers and plastics. Polymers with polar pendent groups are used as coatings and adhesives.

The free energy equation, (6.1), is the overall expression that describes in thermodynamic terms if certain events, such as mixing, solubility, and reactions, will occur. In reactions described in Chapters 6 through 8, a weaker pi bond is broken forming a stronger sigma bond. Thus, the energy or enthalpy of the process, ΔH , favors polymer formation. The reactions are highly exothermic. The change from monomers to polymers results in a decrease in disorder or increase in order with the entropy term, ΔS , working against the reaction occurring. These addition reactions occur with the enthalpy term overcoming the entropy term.

$$(6.1) \quad \Delta G = \Delta H - T\Delta S$$

In contrast to the slow step-reaction polymerizations discussed in Chapter 5, chain polymerizations are usually rapid, and the initiation species continues to propagate until termination. Thus, in the extreme case, a single initiation species could be produced, which would produce one high molecular chain, leaving all of the other monomer molecules unchanged. In any case, the concentration of monomer, which is usually a derivative of ethylene, decreases continuously throughout the reaction. In contrast to stepwise polymerization, the first species produced is a high molecular polymer.

A kinetic chain reaction usually consists of at least three steps, namely, (1) initiation, (2) propagation, and (3) termination. The initiator may be an anion, a cation, a free radical, or a coordination catalyst. While coordination catalysts are important commercially, the ionic initiators will be discussed first in an attempt to simplify the discussion of chain-reaction polymerization.

In almost all of the polymerizations described in this chapter, there is a sensitive and critical balance between the activity of the catalyst and polymerization. For instance, if the catalyst is too active, it may bind at unwanted sites, including the solvent. If the catalyst complex is not sufficiently active, then ready initiation does not occur. The choice of the solvent is also important. Some solvents will react with the catalysts binding it rather than allowing the catalyst to initiate the desired polymerization. Others may *hold* the catalyst complex together rather than allow the catalyst to initiate polymerization. Still, others may not allow the catalyst complex to form. As in much of science, the precise ingredients and conditions were developed through a combination of intuition, science, art, and research. This process continues.

While most vinyl monomers undergo free radical polymerization (Chapter 7), a smaller number undergo ionic polymerization. Cationic polymerizations require monomers that have electron releasing groups such as an alkoxy, phenyl, or vinyl group. Anionic polymerization occurs with monomers containing electron-withdrawing groups such as carboxyl, nitrile, or halide. This selectivity is due to the strict requirements for stabilization of anionic and cationic species.

Compared with free radical polymerizations, ionic polymerizations are not as well defined. Reactions can use heterogeneous initiators, and they are usually quite sensitive to the presence of impurities. Thus, kinetic studies are difficult and the results are sensitive to the particular reaction conditions. Further, the rates of polymer formation are more rapid.

Cationic and anionic polymerizations are similar. Both involve the formation and propagation of ionic species. While high-energy, low-stability, ions would be expected to react with most double bonds, ionic species that are stable enough to propagate are difficult to form and are easily destroyed. The *energetic window* that allows the formation of such charged species is narrow. While polar solvents might be desirable to solvate the ions, and hence help stabilize them, they often cannot be used. Some polar solvents, such as water and alcohols, react with and destroy most ionic initiators. Other polar solvents, such as ketones, prevent initiation because of the formation of stable complexes with the initiators. Ionic polymerizations are therefore conducted in low or moderately polar solvents, such as hexane and ethylene dichloride.

By bulk, almost all vinyl polymers are made by four processes (Table 6.1)—free radical (>50%), complex coordinate (12%–15%), anionic (10%–15%), and cationic (8%–12%). Three of these techniques are covered in this chapter.

Chain growth polymerization: General—The next three chapters will deal with polymers formed from chain growth polymerization. Chain growth polymerization is also called addition polymerization and is based on free radical, cationic, anionic, and coordination reactions where a single initiating species causes the growth of a polymer chain.

The kinetic chain reaction typically consists of three steps—initiation, propagation, and termination. The initiators for free radical, anionic, and cationic polymerizations are organic radicals, carbanions (anionic polymerizations), and carboniums (cationic polymerizations). Chain growth is exothermic with the polymerization mainly controlled by the steric and resonance factors associated with the monomer. Generally, the less resonance stabilization in the growing chain,

TABLE 6.1 Major Techniques Used in the Production of Important Vinyl Polymers

Free radical	Low-density polyethylene
	Poly(vinyl chloride)
	Poly(vinyl acetate)
	Polyacrylonitrile and acrylic fibers
	Poly(methyl methacrylate)
	Polyacrylamide
	Polychloroprene
	Poly(vinyl pyridine)
	Styrene-acrylonitrile copolymers
	Polytetrafluoroethylene
	Poly(vinylene fluoride)
	Acrylonitrile-butadiene-styrene copolymers
	Ethylene-methacrylic acid copolymers
	Styrene-butadiene copolymers
	Nitrile rubber
	Polystyrene
Cationic	Polyisobutylene
	Butyl rubber
	Polyacetal
Anionic	Thermoplastic olefin elastomers (copolymers of butadiene, isoprene, and styrene)
	Polyacetal
Complex	High-density polyethylene
	Polypropylene
	Polybutadiene
	Polyisoprene
	Ethylene-propylene elastomers

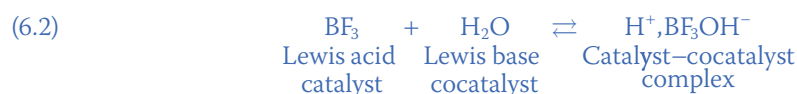
the more exothermic the reaction. Also, the greater the steric factors for the reactants, the less exothermic the polymerization. In all three major chain growth polymerizations, the growing site is typically the end, which offers greater resonance stabilization and greater steric hindrance. In general, the nonsubstituted vinyl site is initially attacked by the growing charged end of the growing chain or initiator as illustrated by Equations 6.3 and 6.4 for cationic polymerizations and 6.23 and 6.25 for anionic polymerizations.

6.1 CATIONIC POLYMERIZATION

6.1.1 KINETICS OF CATIONIC POLYMERIZATION

The art of cationic polymerization, like that of many other types of polymerization, is at least a century old. However, the mechanisms for these reactions have only recently become better understood.

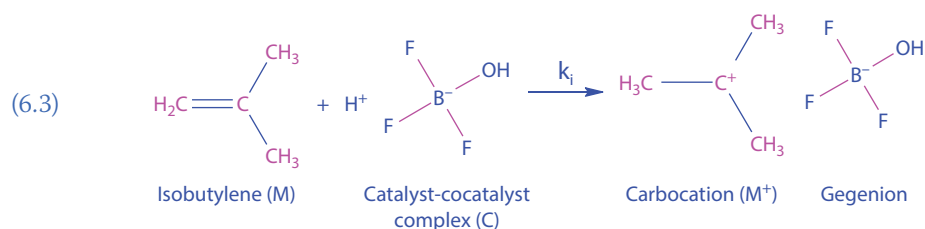
The first species produced in cationic polymerizations are carbocations, and these were unknown as such prior to World War II. It is now known that pure Lewis acids, such as boron trifluoride and aluminum chloride, are not effective as initiators. A trace of a proton-containing Lewis base, such as water, is also required. The Lewis base coordinates with the electrophilic Lewis acid and the proton is the actual initiator. Since cations cannot exist alone, they are accompanied by a “counterion,” also called a “gegenion” (Equation 6.2).



Because the required activation energy for ionic polymerization is small, these reactions may occur at very low temperatures. The carbocations, including the macrocarbocations, repel one another, hence, chain termination does not generally occur by combination but is usually the result of reaction with impurities.

Both the initiation step and the propagation step are dependent on the stability of the carbocations. Isobutylene (the first monomer to be polymerized commercially by ionic initiators), vinyl ethers, and styrene have been polymerized by this technique. The order of activity for olefins is $\text{Me}_2\text{C}=\text{CH}_2 > \text{MeCH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$, and for para-substituted styrenes the order for the substituents is $\text{Me}-\text{O} > \text{Me} > \text{H} > \text{Cl}$. The mechanism is also dependent on the solvent as well as the electrophilicity of the monomer and the nucleophilicity of the gegenion. Rearrangements may occur in ionic polymerizations.

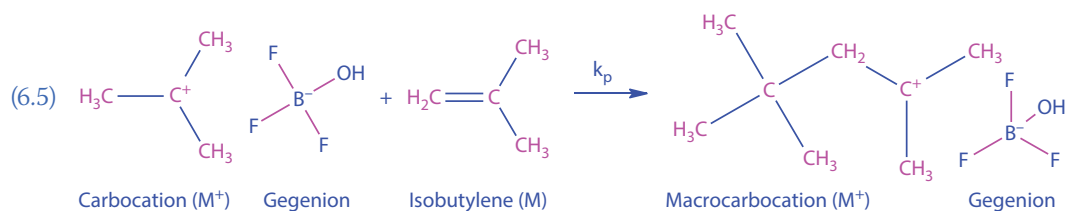
The rate of initiation (R_i) for typical cationic reactions is proportional to the concentration of the monomer $[\text{M}]$ and the concentration of the catalyst–cocatalyst complex $[\text{C}]$, which is given as follows:



$$(6.4) \quad R_i = k_i [\text{C}][\text{M}]$$

Propagation, or chain growth, takes place in a head-to-tail configuration as a result of resonance stabilization and steric factors by carbocation (M^+) addition to another monomer molecule. The head stabilizes the cation best, so it is the growing site while the least sterically hindered site is the site for attack by the cation resulting in the head-to-tail arrangement. The rate constant for

growth is essentially independent of chain length so is the same for all propagation steps and is influenced by the dielectric constant of the solvent. The rate is fastest in solvents with high dielectric constants, promoting separation of the carbocation-gegenion pairs. The chemical and kinetic equations for this are as follows:

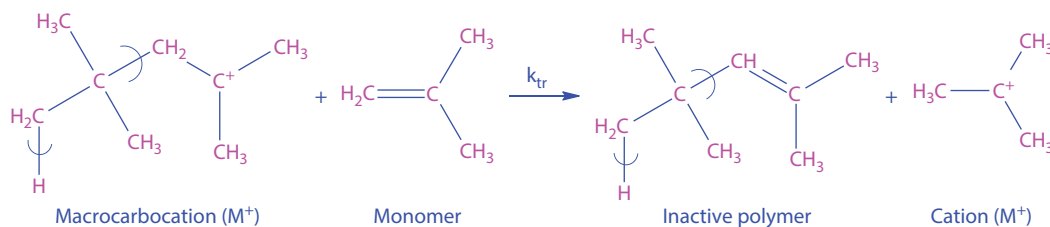


(6.6)
$$R_p = k_p [M][M^+]$$

The termination rate R_t , assumed to be a first-order process, is simply the dissociation of the macrocarbocation-gegenion complex forming BF_3 and H_2O and the now neutral “dead” polymer chain. This is expressed as follows:

(6.7)
$$R_t = k_t [M^+]$$

Termination may also occur by chain transfer, where a proton is transferred to a monomer molecule, leaving a cation that can serve as an initiator. The DP is equal to the kinetic chain length (ν) when chain transfer occurs. The chemical and kinetic equations for termination via chain transfer are as follows:



(6.9)
$$R_{tr} = k_{tr} [M][M^+]$$

It is experimentally found that the rate of initiation equals the rate of termination, and since the propagation step is so rapid, the number of growing chains is constant. Since it is difficult to determine values for some members of the kinetic expressions, including $[M^+]$, the following approach is normally taken to eliminate the need for determining $[M^+]$. Since there is a steady state of growing chains, the rate of initiation is equal to the rate of termination, giving $R_i = R_t$, and solving for $[M^+]$ gives the following:

(6.10)
$$k_i [C][M] = k_t [M^+], \text{ therefore}$$

(6.11)
$$[M^+] = \frac{k_i [C][M]}{k_t}$$

This expression of $[M^+]$ is substituted into the propagation rate expression Equation 6.6 resulting in the following equation:

(6.12)
$$R_p = k_p [M][M^+] = \frac{k_p k_i [C][M]^2}{k_t} = k [C][M]^2$$

For termination by chain transfer we have

$$(6.13) \quad k_i[C][M] = k_t[M][M^+]$$

and

$$(6.14) \quad [M^+] = \frac{k_i[C][M]}{k_t[M]} = \frac{k_i[C]}{k_t}$$

giving

$$(6.15) \quad R_p = k_p[M][M^+] = \frac{k_p k_i[C][M]}{k_t} = k'[C][M]$$

The \overline{DP} can also be described when internal dissociation is the dominant termination step, given as follows:

$$(6.16) \quad \overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M][M^+]}{k_t[M^+]} = k''[M]$$

But if chain transfer is the dominant termination step, then

$$(6.17) \quad \overline{DP} = \frac{R_p}{R_{tr}} = \frac{k_p[M][M^+]}{k_{tr}[M][M^+]} = \frac{k_p}{k_{tr}} = k''$$

It is important to note that regardless of how termination occurs, the molecular weight is independent of the concentration of the initiator. However, the rate of ionic chain polymerization is dependent on the dielectric constant of the solvent, the resonance stability of the carbonium ion, the stability of the gegenion, and the electropositivity of the initiator.

The rates of all single step reactions increase as the temperature increases. But this may not be true for the *net effect* for multistep reactions such as those involved with multistep polymerizations, here the cationic polymerization. For cationic polymerizations, the activation energies are generally of the order $E_{tr} > E_i > E_p$. Remembering that the description of the specific rate constant is

$$(6.18) \quad k = Ae^{-E_a/RT}$$

The overall or *net* activation energy for chain growth from Equation 6.12 is

$$(6.19) \quad E_{(overall)} = E_p + E_i - E_{tr}$$

And for chain length from Equation 6.17, it is

$$(6.20) \quad E_{(overall)} = E_p - E_{tr}$$

For many cationic polymerizations, the net activation is negative, using the relationships given in Equation 6.12, so that the overall rate of polymerization decreases, for these cases, as the temperature is increased. Further, using Equation 6.17 and since $E_{tr} > E_p$, the overall degree of polymerization decreases as the temperature is increased. This is pictured in Figure 5.4.

6.1.2 POLY(VINYL ISOBUTYL ETHER)

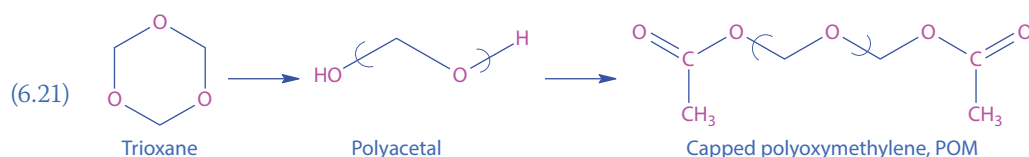
The cationic polymerization of vinyl isobutyl ether at -40°C produces stereoregular polymers. *Poly(vinyl isobutyl ether)* has a low T_g and is used as an adhesive and as an impregnating resin. This production of stereoregular structures has been known for some time and is especially

strong for vinyl ethers. Several general observations have been noted. First, the amount of stereoregularity is dependent on the nature of the initiator. Second, stereoregularity increases with a decrease in temperature. Third, the amount and type (isotactic or syndiotactic) is dependent on the polarity of the solvent. For instance, the isotactic form is preferred in nonpolar solvents, but the syndiotactic form is preferred in polar solvents.

6.1.3 POLYOXYMETHYLENE

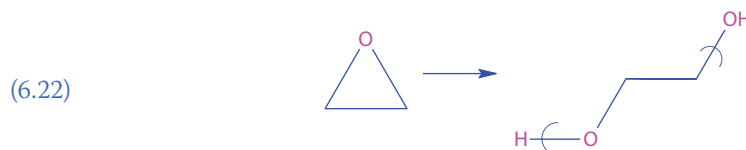
Commercial polymers of formaldehyde are also produced using cationic polymerization. The polymer is produced by ring opening of trioxane. Since the polyacetal, *polyoxymethylene* (POM), is not thermally stable, the hydroxyl groups are esterified (capped) by acetic anhydride. The commercial polymer is a strong engineering plastic. Engineering plastics typically have higher modulus and higher heat resistance than general purpose plastics.

Another stable polyacetal (POM; Celcon) is produced by the cationic copolymerization of a mixture of trioxane and dioxolane.



6.1.4 POLY(ETHYLENE OXIDE)

Many cyclic ethers have been polymerized using cationic polymerization. The tendency for ring cleavage decreases as the size of the ring increases. In fact, the six-membered ring oxocyclohexane is so stable that it does not polymerize even in the presence of a promoter. Ethylene oxide (also called oxirane) polymerizes forming *poly(ethylene oxide)* (PEO, also known as *poly(ethylene glycol)*) (6.22) in the presence of acids such as sulfuric acid, producing a wide range of chain-sized polymers sold under various trade names including Carbowax and Polyox. PEO is also used in cosmetics and pharmaceuticals (as water-soluble pill coatings and capsules). This is covered in greater detail in Section 5.11.



6.1.5 POLYTERPENES AND RELATED POLYMERS

Polyterpenes, coumarone-indene resins, and the so-called petroleum resins are produced commercially using cationic polymerization. These are used as additives for rubber, coatings, floor coverings, and adhesives.

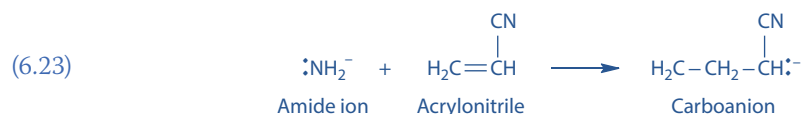
6.2 ANIONIC POLYMERIZATION

6.2.1 KINETICS OF ANIONIC POLYMERIZATION

Anionic polymerization was used to produce synthetic elastomers from butadiene at the beginning of the twentieth century. Initially, alkali metals in liquid ammonia were used as initiators, but by the 1940s they were replaced by metal alkyls such as *n*-butyllithium. In contrast to vinyl

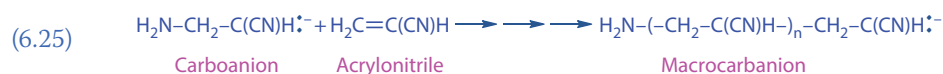
monomers with electron-donating groups polymerized by cationic initiators, vinyl monomers with electron-withdrawing groups are more readily polymerized using anionic polymerization. Accordingly, the order of activity using an amide ion initiator is acetonitrile > methyl methacrylate > styrene > butadiene.

The chemical and kinetic relationships for the anionic polymerization of acrylonitrile follow the same three major steps found in cationic polymerizations—namely, initiation, propagation, and termination.



$$(6.24) \quad R_i = k_i [C][M]$$

where $C = \text{:NH}_2^-$



$$(6.26) \quad R_p = k_p [M][M^-]$$

with termination occurring through solvent transfer gives



$$(6.28) \quad R_{tr} = k_{tr} [\text{NH}_3][M^-]$$

As in the case with cationic polymerizations, the number of growing chains is constant so that a steady state exists such as the $R_i = R_{tr}$. This is useful because it is difficult to determine the concentration of $[M^-]$ so that it can be eliminated as follows:

$$(6.29) \quad k_i [C][M] = k_{tr} [\text{NH}_3][M^-]$$

and

$$(6.30) \quad [M^-] = \frac{k_i [C][M]}{k_{tr} [\text{NH}_3]}$$

Substitution into Equation 6.26 gives

$$(6.31) \quad R_p = k_p [M][M^-] = \frac{k_p [M] k_i [C][M]}{k_{tr} [\text{NH}_3]} = \frac{k' [M]^2 [C]}{[\text{NH}_3]}$$

$\overline{\text{DP}}$ can be described as follows:

$$(6.32) \quad \overline{\text{DP}} = \frac{R_p}{R_{tr}} = \frac{k_p [M][M^-]}{k_{tr} [\text{NH}_3][M^-]} = \frac{k' [M]}{[\text{NH}_3]}$$

Thus, the rate of propagation and the molecular weight are both inversely related to the concentration of ammonia.

Using the same approach we did with the cationic polymerization, we have for the rate of propagation

$$(6.33) \quad E_{(\text{overall})} = E_p + E_i - E_{\text{tr}}$$

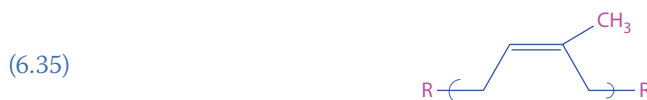
and for the dependence of chain length we have

$$(6.34) \quad E_{(\text{overall})} = E_p - E_{\text{tr}}$$

The activation energy for chain transfer is larger than the activation energy for propagation. The overall activation energy is about 160 kJ/mol. The reaction rate increases and molecular weight decreases as the temperature is increased as shown in Figure 5.4. The reaction rate is dependent on the dielectric constant of the solvent and the degree of solvation of the gegenion. Weakly polar initiators, such as Grignard's reagent, may be used when strong electron-withdrawing groups are present on the monomer, but monomers with less electron-withdrawing groups require more highly polar initiators such as *n*-butyllithium.

6.2.2 CIS-1,4-POLYISOPRENE

Synthetic *cis*-1,4-*polyisoprene* (6.35) is produced at an annual rate of about 100,000 tons by the anionic polymerization of isoprene when a low dielectric solvent, such as hexane and *n*-butyllithium, is used. But when a stronger dielectric solvent, such as diethylether, is used along with *n*-butyllithium, equal molar amounts of *trans*-1,4-polyisoprene and *cis*-3,4-polyisoprene units are produced.



The formation of stable macroanions produces what Szwarc has called "living polymer." These macroanions or macrocarbanions have been used to produce block copolymers such as Kraton. Kraton is an ABA block copolymer of styrene (A) and butadiene (B). Termination is brought about by addition of water, ethanol, carbon dioxide, or oxygen.

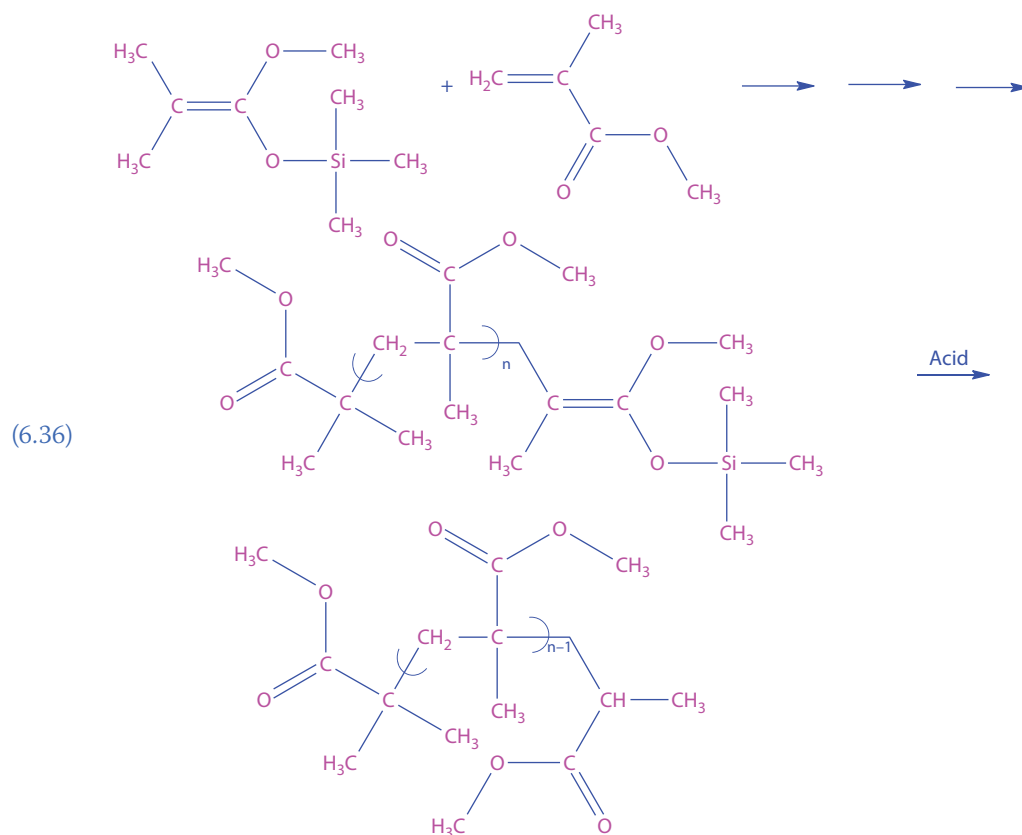
6.2.3 LIVING POLYMERS

Living polymers are generally characterized by (a) an initiation rate that is much larger than the polymerization rate, (b) a polymer molecular weight that is related to [monomer]/[initiator], (c) a linear molecular weight-conversion relationship, (d) a narrow-molecular-weight range, and (e) stabilization of the living end groups allowing the formation of telechelics, macromers, block copolymers, and star polymers.

Group transfer polymerizations make use of a silicon-mediated Michael addition reaction. They allow the synthesis of isolatable, well-characterized living polymers whose reactive end groups can be converted into other functional groups. It allows the polymerization of alpha- or beta-unsaturated esters, ketones, amides, or nitriles through the use of silyl ketenes in the presence of suitable nucleophilic catalysts such as soluble Lewis acids, fluorides, cyanides, azides, and bifluorides, HF_2^- .

As the polymerization occurs, the reactive ketene silyl acetal group is transferred to the head of each new monomer as it is added to the growing chain (Equation 6.36). Similar to anionic polymerization, the molecular weight is controlled by the ratio of the concentration of monomer to initiator. Reactions are generally carried out at low temperatures (about 0°C–50°C) in organic liquids such as tetrahydrofuran (THF). Compounds with *active* hydrogen atoms such as water

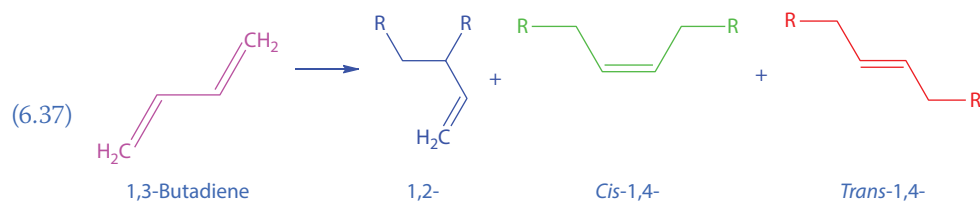
and alcohols will stop the polymerization, and their presence in even small amounts will curtail polymer chain length. Under the right conditions, polymerization will continue until all the monomer has been used up.



The trimethylsiloxy end group is a *living* end, which continues to add units as long as a monomer is available or until it is neutralized.

6.3 STEREOREGULARITY AND STEREOGEOMETRY

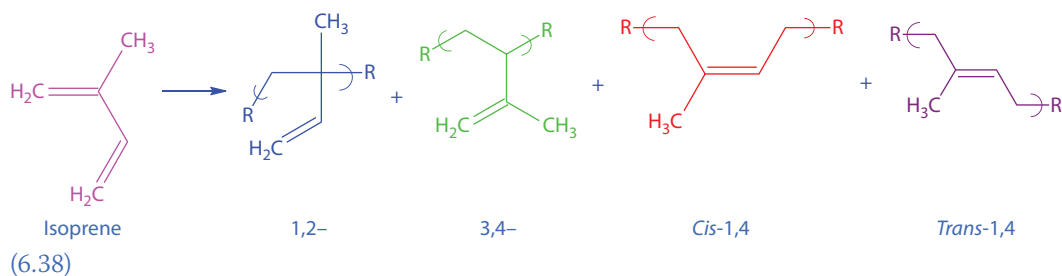
As noted in Chapter 2, there exists stereogeometry and stereoregularity in polymers. These differences have profound effects on the physical and, to a lesser degree, chemical properties of the polymers produced from the same monomer. Three possible units can be formed from the polymerization of butadiene as shown in the following equation:



For isoprene, there are four possible units formed (6.38).

As shown in Figure 2.5, there are three possible stereoregular forms for monosubstituted vinyl polymers. These are isotactic, all of the pendant groups are on one side of the chiral

carbon; syndiotactic, the pendant groups appear on alternate sides of the chiral carbon; and atactic, some mixture of geometries about the chiral carbon.



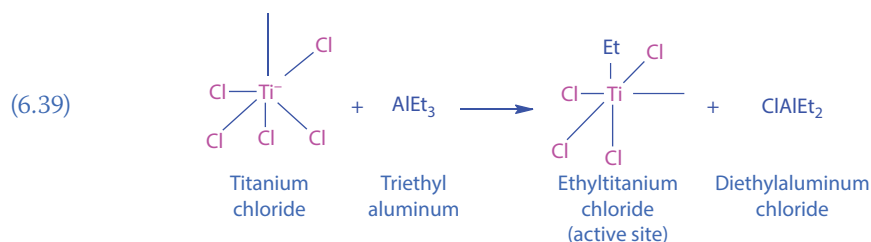
It is important to realize that polymer configuration and conformation are related. Thus, there is a great tendency for isotactic polymers (configuration) to form helical structures (conformation) in an effort to minimize steric constraints brought about because of the isotactic geometry.

6.4 POLYMERIZATION WITH COMPLEX COORDINATION CATALYSTS

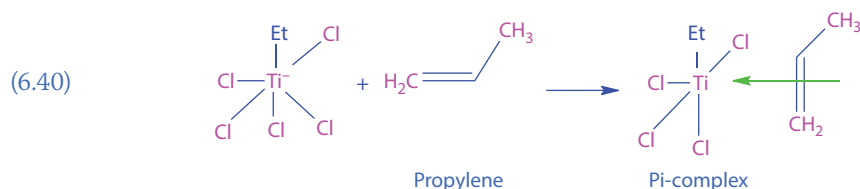
Prior to 1950, the only commercial polymer of ethylene was a highly branched polymer called high-pressure polyethylene where extremely high pressures were used in the polymerization process. The technique for making linear polyethylene (PE) was discovered by Marvel and Hogan and Banks in the 1940s and 1950s and by Nobel Laureate Karl Ziegler in the early 1950s. Ziegler prepared high-density polyethylene (HDPE) by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Another Nobel Laureate, Giulio Natta, used Ziegler's complex coordination catalyst to produce crystalline, stereoregular polypropylene (sPP). These catalysts are now known as Ziegler–Natta (or Natta–Ziegler) catalysts (ZNCs).

In general, a ZNC is a combination of a transition metal compound from Groups IVB (4) to VIIB (10) and an organometallic compound of a metal from Groups IA (1) to IIIA (13) in the periodic table. It is customary to refer to the transition metal compounds as the catalyst (because reaction occurs at the transition metal atom site) and the organometallic compound as the cocatalyst.

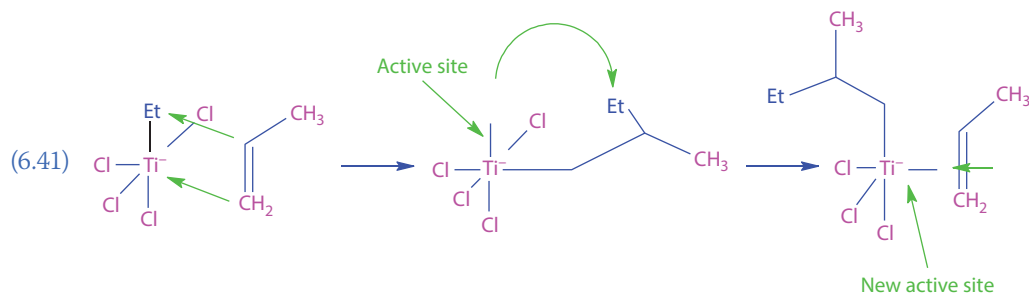
Here, we will use titanium to illustrate the coordination polymerization process. Several exchange reactions between catalyst and cocatalyst occur with Ti(IV) reduced to Ti(III). The extent and kind of stereoregulation can be controlled through a choice of reaction conditions and catalyst/cocatalyst. The titanium salt is present as a solid. The precise mechanism probably varies a little depending on the catalyst/cocatalyst and reaction conditions. Here, we will look at the polymerization of propylene using titanium chloride and triethylaluminum. In general, a monomeric molecule is inserted between the titanium atom and the terminal carbon atom in a growing chain. Propagation occurs at the solid titanium salt surface—probably at defects, corners, and edges. The *last added* monomer is always the terminal group on the chain. Triethylaluminum reacts with the titanium-containing unit producing ethyltitanium chloride as the active site for polymerization.



The propylene forms a pi-complex with the vacant d-orbital of titanium as shown in the following equation:



The ethyl group transfers to the propylene opening up a new active site. The growing chain transfers to the site vacated by the ethyl group creating a new active site that attracts, through pi-interactions, another propylene monomer. This sequence is shown in (6.41). The edges of the solid titanium salt are believed to help provide the contour necessary to form the stereoregular chains.



Most vinyl monomers give a predominance of the isotactic product. Typically, the more exposed the catalytic site, the less the stereoregularity of the resulting polymer. Isotactic PP is produced using this technique as is HDPE.

The versatility of such stereoregulating systems is demonstrated in the polymerization of 1,3-butadiene where all four of the potential structures—isotactic-1,2-, syndiotactic-1,2-, *trans*-1,4, and *cis*-1,4—can be synthesized in a relatively pure form using different catalyst systems.

6.5 SOLUBLE STEREOREGULATING CATALYSIS

The 1940s were a time of studying the kinetics and mechanism of production of vinyl polymers that took *center stage* in the 1950s. The 1950s incubated the solid-state stereoregulating catalysis that spawned a chemical revolution with the synthesis of stereoregular vinyl polymers in the 1960s. The 1980s and early 1990s served as a foundational time for soluble stereoregulating catalysis spawning another revolution related to the production of vinyl polymers with enhanced properties.

The solid-state stereoregulating catalysts *suffered* from at least three problems. First, while stereoregular polymers were formed with good control of the stereochemistry, polymer properties still fell short of the predicted (upper limit) values. This was probably due to the presence of the associated solid catalyst structure that accompanies the active catalytic site. This *excess baggage* restricts the motion of the growing chains so that stereoregular control was good, but the tendency to form good secondary structures was interrupted.

Second, in many cases the solid-state catalysis were incorporated, as contaminants, within the growing polymer making an additional purification step necessary in the polymer processing to rid the polymer of this undesired material.

Third, many solid-state catalysts offered several *active polymerization sites* due to differences in the precise structure at and about the active sites. This resulted in an average stereoregular product being formed.

The new soluble catalysts offer a solution to these three problems. First, the *smaller* size of the active site, and associated molecules, allows the growing chains to *take advantage* of a natural

tendency for the growing polymer chain to form a regular helical structure (in comparison to polymers formed from solid-state catalysts).

Second, the solution catalysts allow the synthesis of polymers that contain little or no catalytic agents, allowing the elimination of the typical additional cleanup steps necessary for polymers produced from solid-state catalysts.

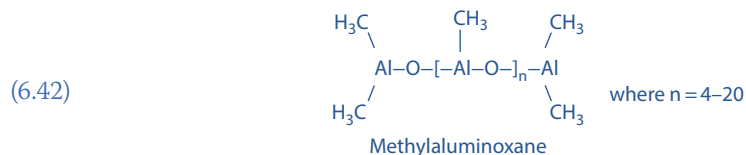
Third, the newer soluble catalytic sites are homogeneous offering the same electronic and stereo-structure allowing the synthesis of more stereoregular-homogeneous polymers.

The new soluble stereoregulating polymerization catalysts require the following three features:

1. A metal atom (active) site
2. A cocatalyst or counterion
3. A ligand system

While the major metal site is zirconium, other metals have been successfully used including Ti, Hf, Sc, Th, and rare earths (such as Nd, Yb, Y, Lu, and Sm). Cyclopentadienyls (Cp's) have been the most commonly used ligands though a number of others have been successfully employed including substituted Cp's and bridged Cp's. The most widely used metal–ligand grouping is zirconocene dichloride. (Zirconocene dichloride has a distorted tetrahedral geometry about Zr).

Methylaluminoxane (6.42) (MAO) is the most widely utilized counterion. MAO is an oligomeric material with the approximate structure given as (6.42).



It is believed that MAO plays several roles. MAO maintains the catalyst complex as a cation, but doing so without strongly coordinating to the active site. It also alkylates the metallocene chloride, replacing one of the chloride atoms with an alkyl group and removing the second chlorine, thus creating a coordinately unsaturated cation complex, Cp_2MR^+ . As an olefin approaches the ion pair containing the active metal, a metallocene-alkyl-olefin complex forms. This complex is the intermediate stage for the insertion of the monomeric olefin into a growing polymer chain.

The structure of the catalyst complex controls activity, stereoselectivity, and selectivity toward monomers. The catalyst structure is sensitive to Lewis bases such as water and alcohols encouraging the use of strongly oxyphilic molecules, such as MAO, to discourage the inactivation (poisoning) of the catalyst.

These soluble catalysts are able to give vinyl polymers that have increased stereogeometry with respect to tacticity as well as allowing the growing chains to form more precise helical structures. Further, the homogeneity of the catalytic sites also allows for the production of polymers with narrow-molecular-weight *spreads*.

The summation of these effects is the production of polymers with increased strength and tensile properties. For PE the use of these soluble catalysts allows the synthesis of PE chains with less branching compared to those produced using solid-state catalysts such as the Zeigler–Natta catalysts (ZNCs). PEs produced employing soluble catalysts also show increased properties in comparison to PEs produced by solid catalysts. Table 6.2 gives some comparisons of the PEs produced using the ZNCs with those produced with soluble catalysts.

Values of $\overline{M}_w/\overline{M}_n$ of 2 or less are common for the soluble catalyst systems, whereas values of 4–8 are usual for ZNC systems. The soluble catalyst systems also are able to polymerize a larger number and greater variety of vinyl monomers to form homogeneous polymers and copolymers in comparison to solid catalyst systems.

The active site is a cationic metallocene-alkyl generated by the reaction of a neutral metallocene formed from reaction with excess MAO or other suitable cocatalysts such as a borane Lewis acid. This sequence is shown in Figure 6.1 employing MAO with ethylene to form PE. Initiation and propagation occur through pre-coordination and insertion of the ethylene into the alkyl group-polymer chain. Here, termination occurs through beta-hydride elimination

TABLE 6.2 Comparison of Properties of Polyethylene Using Solid (Ziegler–Natta Catalysts) and Soluble Catalysts

Property	Unit	Soluble	ZNC
Density	g/cm ³	0.967	0.964
Melt index		1.3	1.1
Haze		4.2	10.5
Tensile yield	psi	800	750
Tensile brake	psi	9400	7300
Elongation break	%	630	670

Source: From Pain, C.F., *Proceedings Worldwide Metallocene Conference (Met Con'93)*, Catalyst Consultant Inc., Houston, TX, May 26–28, 1993.

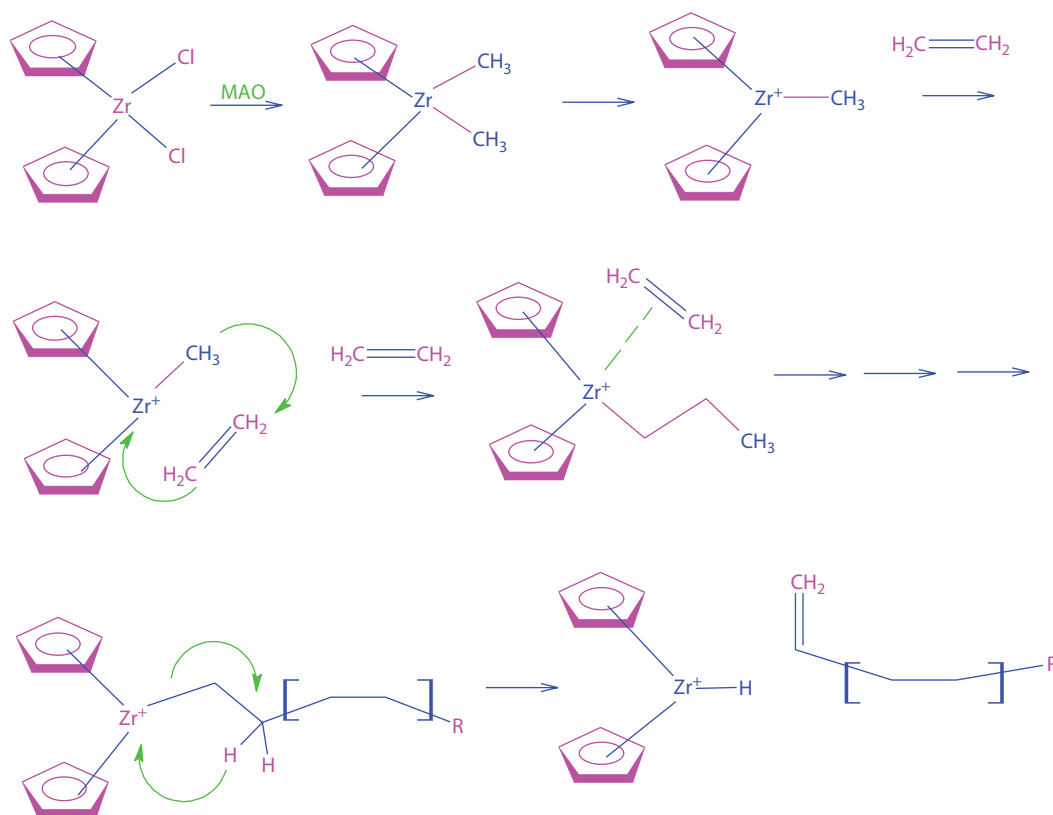


FIGURE 6.1 Proposed mechanism for soluble stereoregulating catalyst polymerizations.

producing a zirconium hydride and a long-chain alpha-olefin. These long-chain alpha-olefins can form linear HDPE or be used as comonomers with monomers such as 1-propylene, 1-hexene, or 1,5-hexadiene to give a variety of branched and linear products. These Group IV B metallocene catalysts are very active producing yields in excess of 1 ton of PE per gram of catalyst per hour with a total efficiency on the order of 25 tons of PE per gram of catalyst.

These catalysis systems are also used to form other hydrocarbon polymers such as a variety of PPs.

A major limitation of such Group IV B metallocene catalysts is that they are very air and moisture sensitive and not tolerant of heteroatom-containing monomers. In the case of heteroatom-containing monomers, the unbonded electron pairs on the heteroatom, such as oxygen, preferentially coordinate to the Lewis acid metal center in place of the carbon–carbon double bond. Some so-called middle- and late-transition-metal organometallics are more tolerant to the

presence of such heteroatoms and can be used as effective cocatalysts. These include some palladium, iron, cobalt, and nickel initiators.

The use of transition and selected main group metal catalysis is increasing with the ability to design special catalytic systems for special polymer architecture and property production. These catalysis systems involve the transition metal as a site for active polymer growth. The new soluble stereoregulating catalysts are one example of these systems. These growing sites may be more or less ionic/covalent depending upon the catalyst used, and such sites are not generally appreciably dissociated as is the case in classical cationic and anionic systems. The metal's ligands can provide both electronic and steric structural control and are generally more robust in comparison to the anionic/cationic systems. Along with many advantages, there are some challenges. Because of their very nature, transition metal initiators can be very complex requiring several synthetic steps; they may be expensive and/or require costly cocatalysts, and control of the particular reaction conditions is very important since small, seemingly subtle changes can be magnified into larger polymer structural changes.

There are an increasingly large number of metal-catalyzed polymerizations including olefin metathesis reactions including *ring-opening metathesis polymerizations*, formation of polyketones from the copolymerization of carbon monoxide, group transfer polymerizations, and step-growth addition/elimination (coupling) polymerizations. The study of metal catalytic sites is a vigorous area of ongoing research.

Polymers produced from single-site catalysts are increasingly being used in the marketplace. As noted earlier, the strength of the materials is increased because of the greater order in the individual polymer chains. For PE this means the number of branches is less and for substituted polymers such as polypropylene this means that the order about the substituted-carbon is increased allowing for a denser, tighter fit of the individual polymer chain segments resulting in increased overall polymer strengths and less permeability for materials.

Use of materials produced from single-site catalysts in areas employing thin films is increasing. For instance, bananas are generally produced at one location and shipped and stored to other locations for sale. Even when picked green, they ripen rapidly when exposed to oxygen. Regular linear low-density polyethylene (LLDPE) is generally employed as a thin film to protect bananas for shipment and storage. Regular LLDPE permits some transfer of oxygen, and because of the somewhat pointed nature of bananas, the film may be punctured. Single-site metallocene-based LLDPE is less permeable and less apt to tear and is now replacing regular LLDPE in this use. Its use is also increasing in the containment of heavier materials such as topsoil and water-purification salt utilizing films. In both cases, thinner films and, consequently, less film material is necessary to give an equal or better job performance. Single site-produced materials also offer better clarity, toughness, and easy sealability.

6.6 POLYETHYLENES

6.6.1 INTRODUCTION POLYETHYLENES

Tupperware was the idea of Earl Silas Tupper, a New Hampshire tree surgeon and plastics innovator (Picture 6.1). He began experimenting with PE during the early part of World War II. In 1947 he designed and patented the famous *Tupper seal* that *sealed in* freshness. In order to close the container, it had to be *burped* to remove air. Tupperware was also bug proof and spill proof, did not rot or rust, and did not break when dropped. Even with all of these advantages, few were sold. Then entered Brownie Wise, a divorced single mother from Detroit that desperately needed to supplement her income as a secretary. Her idea was "Tupperware Parties." By 1951 Tupper had withdrawn all of the Tupperware from the stores and turned over their sales to Brownie Wise with the only source of the ware being through the Tupperware Parties.

The initial synthesis of PE is attributed to many. In 1898 Han von Pechmann prepared it by accident while heating diazomethane. His colleagues Eugen Bamberger and Friedrich Tschirner characterized the white solid as containing methylene units and called it polymethylene. PE, from the ethylene monomer, was probably initially synthesized by M.E.P. Friedrich while a graduate student working for Carl S. Marvel in 1930 when it was an unwanted by-product from the



PICTURE 6.1 Tupperware.

reaction of ethylene and a lithium alkyl compound. In 1932, British scientists at the Imperial Chemical Industries (ICI) accidentally made PE while they were looking at what products could be produced from the high-pressure reaction of ethylene with various compounds. On March 1933, they found the formation of a white solid when they combined ethylene and benzaldehyde under high pressure (about 1400 atmospheres pressure). They correctly identified the solid as PE. They attempted the reaction again, but with ethylene alone. Instead of again getting the waxy white solid, they got a violent reaction and the decomposition of the ethylene. They delayed their work until December 1935 when they had better high-pressure equipment. At 180°C, the pressure inside of the reaction vessel containing the ethylene decreased consistent with the formation of a solid. Because they wanted to retain the high pressure, they pumped in more ethylene. The observed pressure drop could not be totally due to the formation of PE, but something else was contributing to the pressure loss. Eventually, they found that the pressure loss was also due to the presence of a small leak that allowed small amounts of oxygen to enter into the reaction vessel. The small amounts of oxygen turned out to be the right amount needed to catalyze the reaction of the additional ethylene that was pumped in subsequent to the initial pressure loss (another *accidental* discovery). The ICI scientists saw no real use for the new material. By chance, J.N. Dean of the British Telegraph Construction and Maintenance Company heard about the new polymer. He had needed a material to encompass underwater cables. He reasoned that PE would be water resistant and suitable to coat the wire protecting it from the corrosion caused by the salt water in the ocean. In July of 1939, enough PE was made to coat one nautical mile of cable. Before it could be widely used, Germany invaded Poland and PE production was diverted to making flexible high-frequency insulated cable for ground and airborne radar equipment. PE was produced, at this time, by ICI and by DuPont and Union Carbide in the United States.

Some further information about the effort of ICI is of interest to see how industry interacted with academics in the early twentieth century. ICI was interested in high-pressure reactions because academic research showed that high pressure can cause unusual changes in chemical reactivity and because technology had advanced at that time to allow for the attainment of some high pressures. Percy Bridgman, who won the Nobel Prize in Physics in 1946, began his high-pressure efforts in 1905. He attained pressures in the range of 50,000 atmospheres. ICI, about 1928, the same time that DuPont was hiring Carothers, sent two of their research scientists to Amsterdam to work in the lab of A. Michels to study high-pressure reactions. After a 2 year sojourn, they returned to ICI to begin to put to use their newly claimed knowledge. One of the reactants they studied was ethylene. Ethylene was becoming more available as a by-product of

steam cracking of petrochemicals. The scientists mixed ethylene with various chemicals, exposed them to high pressure, and recorded their results. Their *high pressure* was about 1400 atmospheres. For the most part the attempts were failures. In one case they did obtain a white, waxy solid. They analyzed the product, and it has one carbon for every two hydrogens, the empirical formula of CH_2 , the same empirical formula as ethylene. They surmised that the product was PE. They tried to form the product from ethylene alone using higher pressure and temperature and were rewarded with an explosion that shut down the lab for several years. Eventually, they were able to make more of the product and patented the process in 1939.

The early equipment used to make PE was leaky allowing the entrance of air, in particular oxygen. Oxygen, in its ordinary state that we breathe, is a triplet in its ground state meaning it is a diradical. This diradical can abstract a hydrogen from hydrocarbons about it including ethylene forming free radicals. This step is called an initiation step. These free radicals attack, add to, the ethylene monomer forming a radical that in turn is available to add to another ethylene monomer, etc. forming long chains with radical ends. These steps are called propagation steps. Finally, two radicals can react effectively ending the growing process for the chain. This final step is called termination. This sequence is described in Figure 6.2. The topic of free radical polymerization is described in some detail in the following chapter.

The researchers believed they had synthesized linear PE. What they did not know was that the product was branched rather than linear. This is the result of several, at that time unknown, reactions that caused this branching. One of the main sources for this branching is the formation of six-membered rings. Statistics of linear hydrocarbons such as growing PE chains shows that formation of six-member rings is favored resulting in the transfer of the growing radical from the end to within the chain resulting in the formation of four-membered extensions as shown in Figure 6.3.

PE did not receive much commercial use until after the war when it was used in the manufacture of film and molded objects. PE film displaced cellophane in many applications being used

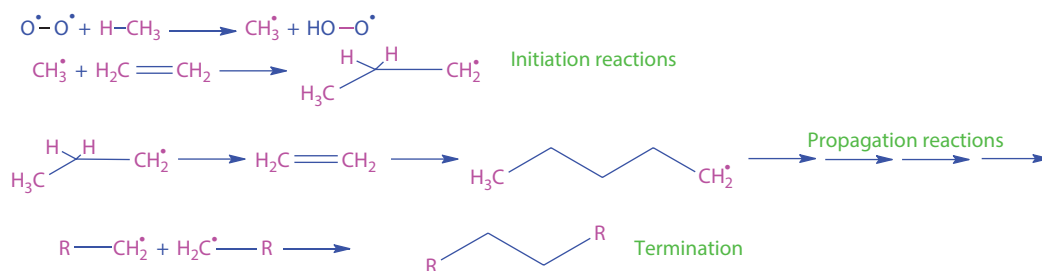


FIGURE 6.2 Free radical polymerization of ethylene.

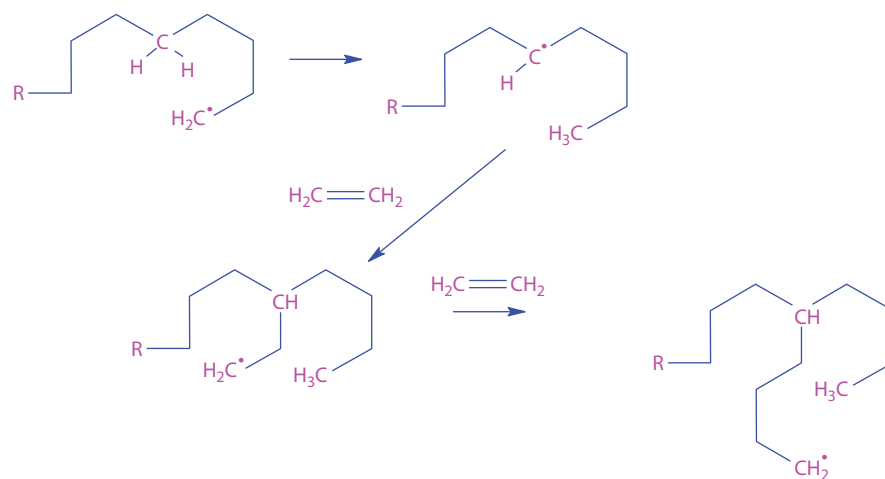


FIGURE 6.3 Formation of branching on growing polyethylene chains.

for packaging produce, textiles, frozen and perishable foods, etc. As noted before, this PE was branched and had a relatively low softening temperature, below 100°C, preventing its use for materials where boiling water was needed for sterilization. The branched PE is called low-density, high-pressure PE because of the high pressures usually employed for its production, and because of the presence of the branches, the chains are not able to closely pack, leaving voids and subsequently producing a material that had a lower density in comparison to low-branched PE. Both HDPE and low-density polyethylene (LDPE) have been employed in the production of Frisbees (Picture 6.2) and other incidental materials such as streamers (Picture 6.3).

Karl Ziegler, director of the Max Planck Institute for Coal Research in Muelheim, Germany, was extending early work on PE attempting to get ethylene to form PE at lower pressures and



PICTURE 6.2 Frisbees are mainly produced using thermoplastic polyethylene by injection molding. Here are Herman, Brooke, Paul, Lydia, and Benjamin Gunter ready for a Frisbee tournament.



PICTURE 6.3 Pompoms with PE streamers and PP name tag.

temperatures than required to produce low-density polyethylene. His group found that certain organometallics prevented the polymerization of ethylene. Along with finding compounds that inhibited PE formation, they found compounds that allowed the formation of PE under much lower pressures and temperatures. Further, these compounds produced a PE that had fewer branches and higher softening temperatures.

Giulio Natta, a consultant for the Montecatini Company of Milan, Italy, applied the Zeigler catalysts to other vinyl monomers such as propylene and found that the polymers had a higher density and higher melting temperature and they were more linear than those produced by the then classical techniques such as free radical-initiated polymerization. Ziegler and Natta shared the Nobel Prize in 1963 for their efforts in the production of vinyl polymers using what we know today as solid-state stereoregulating catalysts.

While many credit Natta and Ziegler as first having produced the so-called high-density PE and stereoregular polyolefins, Phillips' scientists first developed the conditions for producing stereospecific olefin polymers and HDPE. In 1952 John Paul Hogan and Robert Banks discovered that ethylene and propylene polymerized into what we today know as high-density PE and stereoregular PP. As with many other advancements, their initial studies involved other efforts, here to improve fuel yields by investigating catalysts that converted ethylene and propylene to higher-molecular-weight products. They found that chromium trioxide supported on a silica-alumina catalyst produced a hard solid rather than the usual waxy-like PE. They quickly looked at other olefins and soon discovered a crystalline PP, namely a stereoregular PP, specifically isotactic PP (iPP), more about this in Section 6.7.3.

While the common name for the monomer is ethylene, the official name is ethane so that what we know as polyethylene is often referred to as polyethene, or polythene. Even so, the name polyethylene is so entrenched in our common vocabulary it will be employed here. PE can be produced employing radical, anionic, cationic, and ion coordination polymerization. This is a result of the lack of substituents on the ethylene monomer. Each of these different polymerizations results in a different type of PE. Today, there exist a wide variety of *polyethylenes* that vary in the extent and length of branching as well as molecular weight and molecular weight distribution and amount of crystallinity. Some of these are pictured in Figure 6.4. Commercial LDPE typically has between 40 and 150 short alkyl branches for every 1000 ethylene units. It is produced employing high pressure (15,000–50,000 psi) and temperatures (to 350°C). It has a density of about 0.912–0.935. Because of the branching, the LDPE is amorphous (about 50%), and sheets can allow the flow-through of liquids and gasses. Because of the branching and low amount of crystallinity, LDPE has a low melting point of about 100°C making it unsuitable for uses requiring sterilization through use of boiling water. LDPE has a combination of short to long branches, at a rate of about 10 short branches for every long branch.

6.6.2 HIGH-DENSITY POLYETHYLENE

HDPE produced using organometallic catalysts such as the ZNCs or Phillips catalysts have less than 15 (normally within the range of 1–6) short alkyl branches (essentially no long branches) for 1000 ethylene units. Because of the regular structure of the ethylene units themselves and the low extent of branching, HDPE chains can pack more efficiently resulting in a material with greater crystallinity (generally up to 90%), higher density (0.96), and increased chemical resistance, hardness, stiffness, barrier properties, melting point (about 130°C), and tensile strength. Low-molecular-weight (chain lengths in the hundreds) HDPE is a *wax*, while *typical* HDPE is a tough plastic widely used to form many products including *plastic* containers (Picture 6.4).

6.6.3 LINEAR LOW-DENSITY POLYETHYLENE

LLDPE can be produced with less than 300 psi and at about 100°C. It has a density from 0.915 to 0.925 g/mL. It is actually a copolymer of ethylene with about 8%–10% of an alpha-olefin such as 1-butene, 1-pentene, 1-hexene, or 1-octene. Through control of the nature and amount of alpha-olefin, we are able to produce materials with densities and properties between those of LDPE

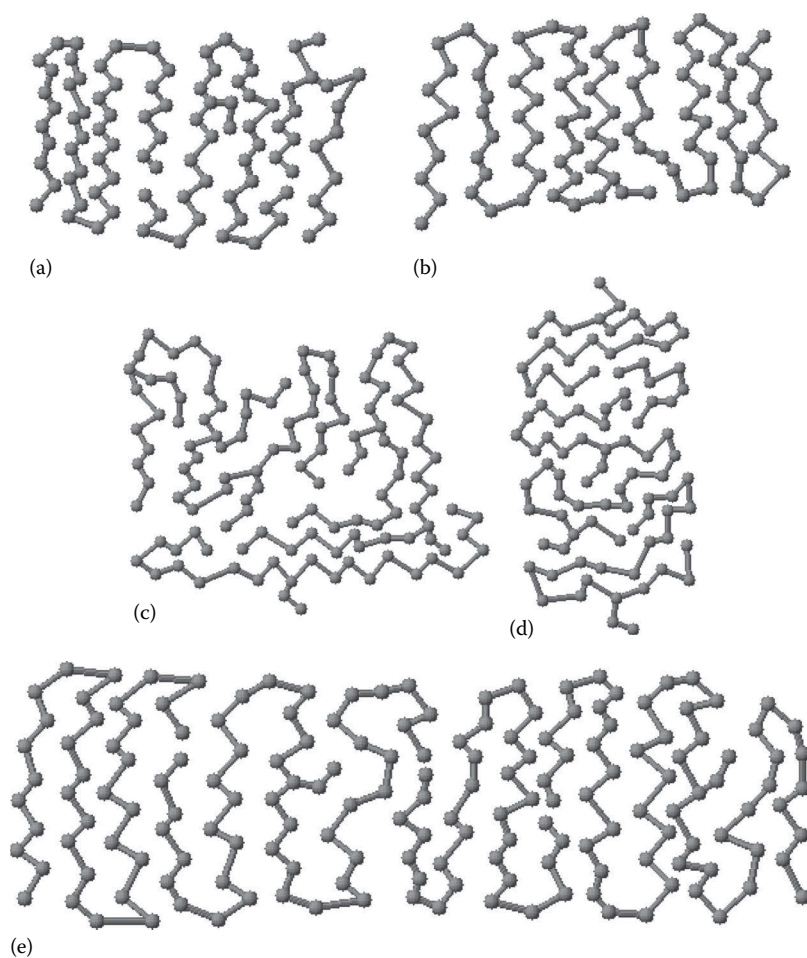


FIGURE 6.4 Ball-and-stick models of high-density polyethylene (a), ultrahigh-molecular-weight polyethylene (b), low-density polyethylene (c), linear low-density polyethylene (d), and ultralinear polyethylene (e).



PICTURE 6.4 HDPE containers.

and HDPE. LLDPE does not contain the long branches found in LDPE. Because of its toughness, transparency, and flexibility, it is used in film applications as packaging for cables, toys, pipes, and plastic streamers and containers.

6.6.4 VERY-LOW-DENSITY POLYETHYLENE

Very-low-density polyethylene (VLDPE) has a density range from 0.88 to 0.915 g/mL. It is largely linear chains with a high amount of short-chain branching generally made by copolymerization of the ethylene with short-chain α -olefins such as 1-butene, 1-hexene, and 1-octene so that it is structurally similar to LLDPE except the α -olefins are generally longer, resulting in a lower density. VLDPE is generally made employing metallocene catalysts.

6.6.5 ULTRAHIGH-MOLECULAR-WEIGHT POLYETHYLENE

Ultra-high-molecular-weight polyethylene (UHMWPE) is an HDPE with chain lengths over 100,000 ethylene units. Because of the great length of the chains, they *intertangle* causing physical cross-links, increasing the tensile strength and related properties of these materials (by comparison, HDPE rarely is longer than 2000 ethylene units). UHMWPE is about 45% crystalline and offers outstanding resistance to corrosion and environmental stress cracking, outstanding abrasion resistance and impact toughness, and good resistance to cyclical fatigue and radiation failure, and with a low surface friction. It is produced utilizing catalyst systems similar to those employed for the production of HDPE (i.e., ZNCs and Phillips catalysts). It has a density of about 0.93.

6.6.6 ULTRALINEAR POLYETHYLENE

Ultralinear polyethylene (ULPE) has recently become available through the use of soluble stereo-regulating catalysts. Along with a decreased amount of short-chained alkyl branching, ULPE has a narrower-molecular-weight spread.

At extremely high-chain lengths, fibers can be made of largely linear PE producing a material that is extremely strong and resistant to punctures and cutting even by scissors. One such product is *Spectra* composed of high molecular weight; about 70,000 units long, PE fibers stretched about 100% to align the chains. Spectra is used in the construction of bullet-resistant vests and surgical gloves where nicking and cutting of surgeon's hands by the sharp instruments is unwelcome. Spectra is said to be 10 times stronger than steel on a weight basis and 35% stronger than aramid fibers such as Kevlar. Like other woven materials, these gloves are vulnerable to punctures by sharp objects such as needles.

6.6.7 CROSS-LINKED POLYETHYLENE

Cross-linked polyethylene (PEX or XLPE) is a medium to HDPE that contains cross-links resulting in a thermoset material. The cross-linking causes a reduced flow for the material and permeability and increased chemical resistance. Because of the good retention and stability toward water, some water pumping systems use PEX tubing since its cross-linking causes the tubing, once expanded over a metal nipple, to return to its original shape resulting in a good connection.

6.6.8 MEDIUM-DENSITY POLYETHYLENE

Medium-density polyethylene (MDPE) has a density between about 0.93 and 0.94 g/mL. It is mainly produced employing ion coordination polymerization. It has good shock and drop resistance.

6.6.9 POLYMETHYLENE

Polymethylene can be produced through several routes including the use of diazomethane or a mixture of carbon monoxide and hydrogen. This polymer has only a little branching.

Space-filling models of amorphous and crystalline linear PE are given in Figure 6.5.

6.6.10 SHOPPING BAGS

Most shopping bags are made from PE, PP, or paper (Picture 6.5). Today there is a move to remove the so-called nongreen plastic bags. A brief comparison of the two is in order. In comparison to paper bags, plastic bags are lighter, stronger, lower cost, and water and chemical resistant. They cost less energy to produce (about 70%), offer less of a carbon dioxide footprint (about 50%), transport, and recycle. When disposed of improperly plastic bags are unsightly and represent a hazard to wildlife and infants. Neither paper (because of lack of oxygen) nor plastic bags decompose in landfills. Both can be recycled. Paper is made from a renewable resource, cellulose from trees. With the move toward poly(lactic acid) bags and woven textile bags, long-term disposal and degradation will become less of a problem. Thus, the answer is not apparent but what is apparent is that we must increase our efforts to recycle and properly dispose of both plastic and paper bags.

Various figures are offered comparing different bags. Table 6.3 contains data compiled from several studies. It is obvious from comparing the figures that the lowest, most favorable, values are found for PE bags. But if we remember that the values are of a single usage and reusable bags are used many times, we see that this is not necessarily the case. We use reusable bags generally 50 times before they become *thread bare* and not usable without recycling. The right column contains values based on 50 uses. We see that these values are lower than for PE bags.

It is well accepted that the history of a polymer, including polymer processing, influences polymer behavior. Some of these influences are just becoming known. Interestingly, as in much of science, once the critical parameters are known on a macrolevel, we are able to better understand them on a molecular and conceptual level. An example that illustrates this involves the

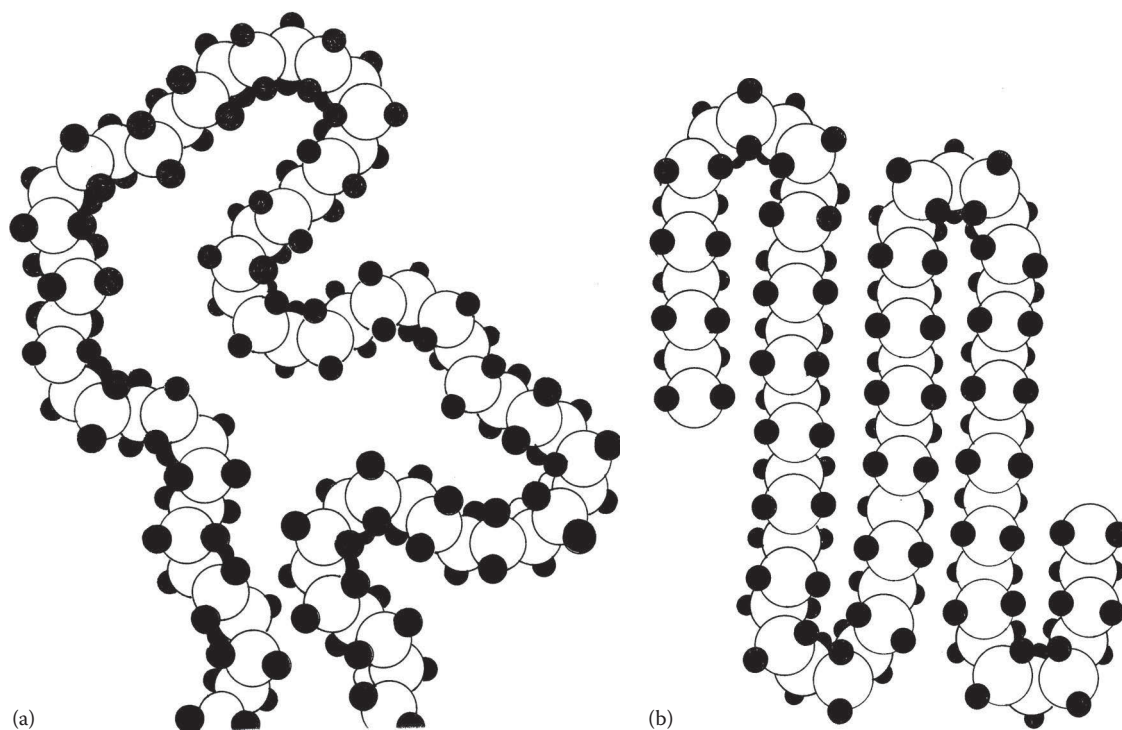


FIGURE 6.5 Space-filling structure of a portion of a linear amorphous (a) and crystalline (b) polyethylene region.



PICTURE 6.5 Typical shopping bags—polypropylene (with the chasing arrows), woven textile (blue and green), and a host of polyethylene bags.

TABLE 6.3 Environmentally Related Values for Different Disposable Bag Materials

Bag Type	Polyethylene	Paper	Reusable Nonwoven Polypropylene	Reusable Polyethylene with 40% Recycled Material	Reusable Nonwoven Polypropylene—50 Uses
Mass (kg)	4	50	40	45	0.8
Nonrenewable energy (GJ)	500	2600	3800	3000	75
Greenhouse emissions (Metric tons CO ₂ equivalent)	0.027	0.08	0.26	0.18	0.0005
Water consumption (Gallon)	40	1000	425	40	8.5

Source: Based on material from C&EN, September, 15, 2014; J. Greene; per 1000 bags for single use.

processing of annealed PE. In general, for most linear PE, micelles and associated spherulites are formed when it is melted and then slowly cooled. If no force is applied during the annealing process (simple melt crystallization), a high amount of force and large deformation are required to break down the initial spherulite structures with reformation occurring along the axis of the pull when high-strength PE rod, film, and sheet are produced. However, if the PE is crystallized under pressure applied in one direction, less energy and lower deformation are required to align the PE spherulites since the spherulites are already partly aligned. In both cases, stretching of the molecular network is required. For the simple melt crystallized PE, the original spherulite structure is destroyed during the deformation followed by the formation of new fibrillar structures. For the pressure-associated annealing process, elongated micelles are formed that largely remain after the deformation process.

LDPE films are nearly clear even though they contain a mixture of crystalline and amorphous regions. This is because the crystalline portions are space filling and not isolated spherulites allowing a largely homogeneous structure with respect to refractive index resulting in a material that is transparent. In fact, the major reason that LDPE films appear hazy or not

completely transparent is because of the roughness of the surface and is not due to the light scattering of the interior material.

Typical uses of the various PEs are the following:

1. UHMWPE—Battery separators; lightweight fibers; permanent solid lubricant materials in railcar manufacture; automobile parts; truck liners; liners to hoppers, bins, and chutes; farm machinery as sprockets, idlers, wear plates, and wear shoes; moving parts of weaving machines and can and bottle handling machines; artificial joints including hip and knee replacements; gears; butcher's chopping boards; sewage-treatment bearings; sprockets; wear shoes; lumbering-chute and sluice and chain-drag liners; neutron shields, also as components in bullet-resistant wear
2. *Typical* HDPE—Blow-molded products, such as bottles, cans, trays, drums, tanks, and pails; injection-molded products including housewares, toys, food containers, cases, pails, and crates; and films, pipes, bags, conduit, wire and cable coating, foam, insulation for coaxial, and communication cables
3. Low-molecular-weight HDPE—Spray coatings, emulsions, printing inks, wax polishes, and crayons
4. LDPE—Packaging products, bags, industrial sheeting, and piping and tubing, films, garbage cans, industrial containers, and household items
5. LLDPE—Telephone jacketing, wire and cable insulation, piping and tubing, drum liners, bottles, and films
6. MDPE—Shrink film, packaging film, and gas pipes and fittings
7. VLDPE—Frozen food and ice bags, food packaging, and stretch wrap

Recently, efforts are underway to form ethylene and, hence, PE, from green chemistry feedstocks—sugar cane—derived ethanol and other natural feedstocks.

Plastomers is the name given to copolymers of ethylene that have a little crystallinity, but are largely amorphous. They are also called very-low-density polyethylene, VLDPE. They are more elastic than LLDPE but less stiff. They are used as a sealing layer in film applications and controlled permeation packaging for vegetables and fruits.

6.7 POLYPROPYLENE

6.7.1 HISTORY

The initial PE, LDPE, was produced employing free radical polymerization. But the methyl group in the propylene monomer is a source of somewhat easily broken hydrogen atoms that compete for the free radical making the free radical polymerization of propylene difficult. This is because of resonance stabilization of the resulting allyl radical, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\cdot$. Thus, polymerization of the propylene monomer awaited developments employing a different mechanism.

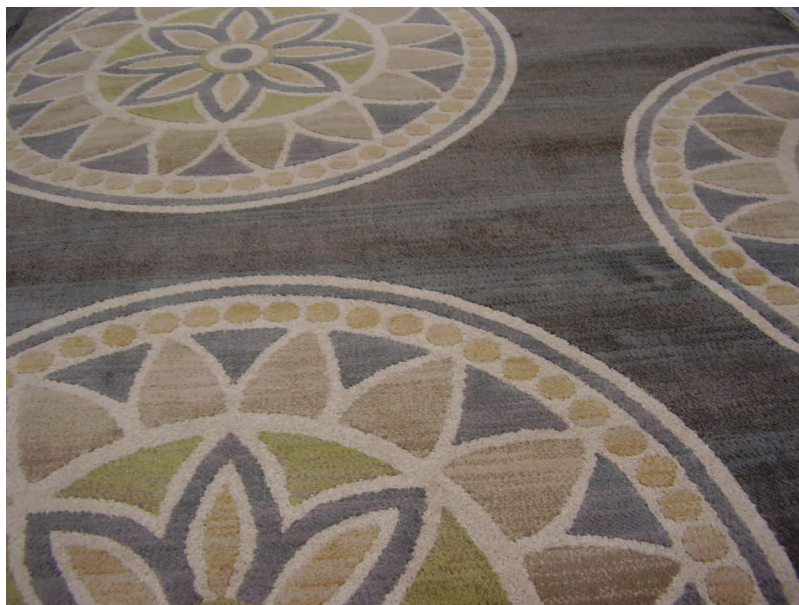
PP is one of the three most heavily produced polymers (Section 1.3). The abundance of PP is the result of the variety of PP produced, its versatility allowing a wide variety of products to be produced, availability of a large feedstock, and inexpensiveness. Today, PP is used in such diverse applications as a *film* in disposable diapers and hospital gowns to geotextile liners, *plastic* applications as disposable and nondisposable containers (Picture 6.6), automotive components, and *fiber* applications such as in carpets, furniture fabrics, and twine.

As a fiber, it forms the basis for vinyl carpets (Picture 6.7). It is difficult to color and typically does not wear well but is inexpensive, and new advances have allowed it to be more easily colored and in texture similar to most other common polyester and nylon rugs. But the feel is less desirable simply because polyester and nylon are less hydrophobic. Vinyl rugs are generally formed using some sort of connective loop construction. Commercial grade rugs wear well. They have good stain resistance but not against oil-based materials since the oil-based contaminants have similar structures to the polyolefin material.

PP is also used to make a number of somewhat mundane objects such as drinking straws (Picture 6.8). The use of PP, rather than the old standby PS, is favored because PS is more brittle



PICTURE 6.6 Plastic PP containers.



PICTURE 6.7 Polyolefin or vinyl (largely polypropylene) rug.

tending to crack more easily. Also, PS is denser than water, while PP is not, so the PS straws tend to sink, while the PP straws do not.

While PP was produced in 1951 by Karl Rehn, it only became commercially available in the late 1950s with the production by Natta and coworkers at Phillips of somewhat stereoregular PP. The first PP was not highly crystalline because the tacticity, a measure of the stereoregularity, was only approximate. But with the use of the Natta–Zeigler and Phillips catalyst systems, PP with greater stereoregularity was produced giving PP with enhanced physical properties such as increased stiffness, better clarity, and a higher distortion temperature. Today, with better catalysts, including the soluble metallocene catalysts, the tacticity has been increased so that PP with 99% isotacticity can be produced. The more traditional Natta–Zeigler catalysts have high catalytic efficiencies with 1 gram of catalysts producing 1 kilogram of PP. This high



PICTURE 6.8 Polypropylene drinking straws.

catalytic efficiency eliminates the need for catalyst removal. Most iPP is made using bulk propylene, either as a gas or as a liquid.

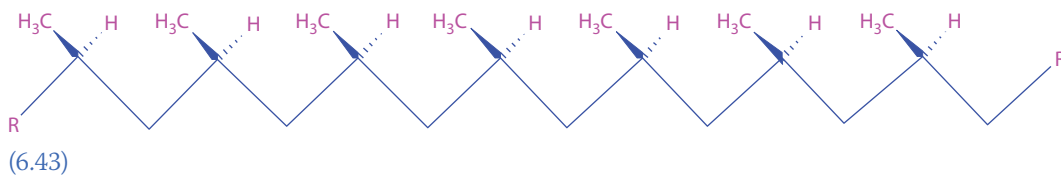
A brief side trip allows some insight into industrial workings. The Phillips Petroleum Company was busily working on ways to improve refinery processes because they were in the 1950s almost solely a fuel company. Two young chemists, John Paul Hogan and Robert L. Banks, were trying to develop catalysts that would act as high-performance gasoline additives when one of the catalysts, mixed with the petroleum propylene present in a pipe, plugged up the pipe with a whitish, taffy-like material. While many companies might have told Hogan and Banks to get back to their original efforts that were the *bread-and-butter* of the company, instead they were told to investigate the formation of this off-white material. At this time, most of the known plastics were either too brittle or softened at too low a temperature for most practical uses. This off-white material, produced from propylene, could be hardened giving a flexible material that melted above 100°C. After some effort, it was discovered that this catalyst could also be used to give a PE that was superior to the *old* PE. Eventually, the *old* PE would be given the name of low-density polyethylene, LDPE, and the new polyethylene the name of high-density polyethylene, HDPE.

In 1953 a patent was applied for covering both the synthesis of PP and PE under the trade name Marlex. Even after a material is discovered, many steps are needed before a product becomes available to the general public. Management was getting glowing reports about the potential for these new materials. Based on these assessments, \$50 million was committed for the construction of a large-scale PE plant at Adams Terminal.

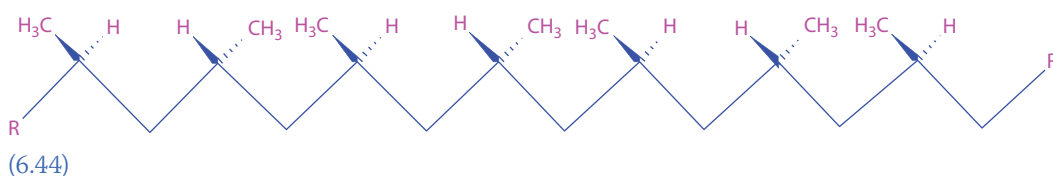
Several things were occurring that are not immediately apparent. First, the great investment of money and time needed to bring a product into the marketplace. At that time \$50 million was a lot of money, on the order of half a billion dollars today. Second, up to that time, technicians with little training were used in much of the chemical industry. The *educated* chemists were kept behind the research benches discovering *new* things. Most of the PhD chemists were, in fact, in universities rather than in industry. (Today, only about 11% of the professional chemists are teaching, the remainder are employed in industry and government.) Because of the sensitivity of the catalyst system used to produce the new polymers, substantially greater training had to be given to workers that dealt with the production of these new polymers. Third, this was a venture into a new arena by Phillips, up to now solely a gasoline-producing company. Finally, while not initially apparent, the catalysts used to produce these new polymers were part of a new group of catalysts being investigated internationally by many companies that allowed the production of so-called stereoregular polymers.

6.7.2 STEREOSPECIFIC STRUCTURES

As noted previously, PP, and other alpha-olefins, can reside in three main stereoregular forms differentiated from one another because of the precise geometry of the methyl group as the polymer is formed. When the methyl groups reside on the same side as one looks down a barrow of the chain, given as follows, it is called isotactic polypropylene or simply iPP.



The methyl group can also exist in alternate positions as shown in the following. This form is called syndiotactic polypropylene or simply sPP.



The third structure consists of mixtures of the syndiotactic and isotactic structures favoring neither structure. This mixture of structures is called the atactic form, atactic PP (aPP), the “a” meaning having nothing to do with. Space-filling models of all three different tactic forms are given in Figure 6.6.

Each particular tactic form has its own physical properties. The syndiotactic and isotactic forms are referred to as stereoregular forms and allow the chains to better fit together giving a material that is crystalline while the aPP is amorphous. Being crystalline causes the polymer to be stronger, denser, less porous to small molecules like water and oxygen, and to have a higher melting temperature. The old PP is of the atactic form and the form synthesized

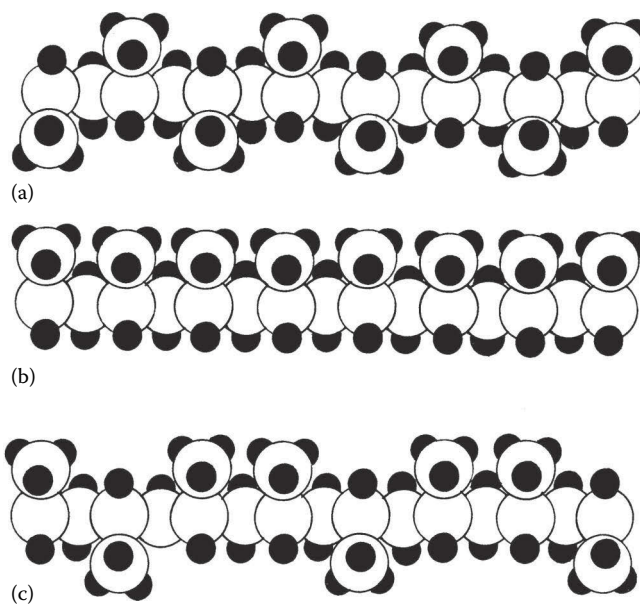


FIGURE 6.6 Space-filling models of syndiotactic (a), isotactic (b), and atactic (c) forms of polypropylene. (My children and now grandchildren believe that the isotactic polypropylene is really a chorus-line of dancing teddy bears.)

by Hogan and Banks is iPP. Only recently, using soluble stereoregulating systems, has sPP become commercially available.

Other groups were working on developing these stereoregulating catalysts. In fact, more research dollars and effort were spent during the 1950s developing these stereoregulating catalysts than that spent on cancer research during that time. The competition was fierce and monetary stakes were high. I was present at one of the initial presentations of the results from a number of different groups. Each group believed that their catalyst system gave the best results and each believed that the product they obtained was the same product that other companies obtained. There were several times during the presentations where the groups would yell at one another and physically wrench the microphone from another speaker calling one another various unkind words. It was later learned that each of the groups had different catalytic systems that gave different products. Thus, the presenters were most probably giving accurate information but based on slightly differing catalyst systems.

6.7.3 EARLY PRODUCTION

As noted previously, several groups were involved in the early development of the stereoregulating catalysts and catalysts that allowed the formation of HDPE and PP. Robert Banks and J. Paul Hogan, working for Phillips, developed a chromium catalyst that was used to form HDPE. They also tried to polymerize propylene using the same catalyst but got only a low yield of crystalline PP. They entered this *failure* in their lab notebooks and moved on to other endeavors. Prior to this, attempts at polymerizing propylene gave only viscous syrups. Because of the work by Banks and Hogan, a patent suit was filed in the United States describing them as the inventor of the production of crystalline PP rather than Natta using Ziegler's catalyst. No patent was allowed to issue until the suit was settled. Litigation lasted 27 years. The litigates included Phillips, DuPont, Hercules, Amoco, and Montedison, the Italian company that sponsored Natta's efforts. Phillips was eventually awarded the patent based on the notebook entry of the *failed* experiment of Banks and Hogan. It pays to record your failures as well as successes. During the 27 years many companies had been producing PP and other stereoregular polymers. The granting of the patent to Phillips allowed Phillips to collect over 1 billion dollars in past royalties from U.S. manufacturers. But foreign companies were exempted as long as they did not sell the material in the United States.

Jumping from a laboratory scale production to mass production is difficult and made especially difficult because of the need to control the structure of the catalyst because only one form of the catalyst gave the desired iPP and PE while other forms would give mixtures of PP and PE structures. The first Marlex pellets came off the production line at the Adams plant, and they were varied in color and size, and off-specification. It was hard for the sales staff to convince buyers that this was the miracle material that they had promised. The realization that the catalysts form was so important became painfully evident. The material was better than the old PE and PP, but it was not as good as that obtained in the laboratory. Warehouse after warehouse of somewhat inferior material was produced with few buyers.

Relief was spelled, not "R-E-L-I-E-F," but rather "H-U-L-A H-O-O-P," which was reinvented by Richard Knerr and Arthur "Spud" Melin (Picture 6.9) who founded the Wham-O company that also reinvented another old toy, the Frisbee. American children fell in love with the hula hoop and the somewhat inferior Phillips material was good enough to give good hula hoops. Demand for these plastic rings was sufficient to take the Adams plant output for a half year and turn it into hula hoops. Phillips president, Paul Endacott, was so pleased that he kept a hula hoop in his office to remind him of his *savior*. By the time that particular wave of hula hoop mania wound down in 1959, the problems in the product line at the Adam terminal were overcome and Marlex had found new markets. One of the first markets was the use of PE and PP baby bottles in hospitals to replace the old glass bottles. The Marlex bottles were less expensive, could be sterilized (remember both the new PE and PP could be heated to boiling, 100°C, without melting) and would not shatter when dropped. The manufacture of Chiffon household liquid detergent took a chance on using plastic bottles rather than glass to hold their detergent. Their success caused other manufacturers to change to the lighter, nonbreakable, and less expensive plastic containers. Today, PP and PE hold the major share of the container market.



PICTURE 6.9 Polypropylene hoop widely popular beginning in the late 1950s when about 100 million hoops were sold in a year.

Copying the tubes used to make the hula hoop, plastic tubing for many varied applications such as connecting air conditioners and ice makers took off. Today, the two most used synthetic polymers are PE and PP. New catalysts and production procedures have allowed the physical properties and varied uses of these *big two* synthetic polymers to be continually increased.

While it was possible to produce sPP employing the Zeigler–Natta solid systems, commercial sPP has only recently become commercial through the use of the soluble metallocene catalysts. These materials have a similar T_g as iPP, but they have a different balance between stiffness and toughness.

Atactic or amorphous forms of PP are also used. Initially, aPP was obtained as a by-product of the production of iPP. As an inexpensive by-product, it is used as a modifier for asphalt, for roofing, and in adhesives. As the effectiveness of catalyst systems becomes better, less aPP is available so that today some aPP is intentionally made for these applications.

While PP is often synthesized employing ZNC, today there exist many other catalyst systems including the soluble catalyst systems described in Section 6.6. Many of these were developed by Walter Kaminsky and coworkers in the 1980s to the 2010s. These catalysts contain a Group IVB metallocene coupled with methylaluminoxane (MAO). Through varying the structure of the metallocene cocatalyst, it is possible to tailor the tacticity of the product. Thus, for PP, the atactic product is formed when the simple zirconocene and hafnocene dichlorides are employed, sPP is produced when a bridged catalyst is employed, and iPP is produced when another bridged catalyst is employed.

6.7.4 FORMS OF POLYPROPYLENE

As noted, PP exists in three major forms associated with tacticity or arrangement of the methyl groups from unit to unit. Focusing only on iPP, at least five crystal forms are known with each form exhibiting different physical properties that are exploited industrially. For many years three crystalline forms known as α , β , and γ were known. In the past two decades, two additional forms were found known as δ and more recently ϵ . The presence of these forms signifies the importance that fine or molecular structure has on the bulk properties of materials and how these different structures, of essentially the same material differing only in the crystal structure, have on the overall physical properties and potential industrial use.

Even after a material is formed through polymerization, its physical properties, derived from changing the molecular structure, can influence the overall structure. For instance, stretching a film tends to orientate the polymer chains. Biaxially stretched or oriented polypropylene is strong and clear resulting in its wide use in producing clear bags and packaging materials. PP is often used in the construction of cold-weather clothing under layers such as long-sleeved shirts and underwear. It is also used in warm-weather wear because of its ability to remove perspiration from the skin. It is used in ropes that can float because of the low density of PP. In low-ventilation areas, it often replaces PVC because it emits less smoke and no dangerous chlorine-containing fumes. It serves as the suture material in Prolene. Because of its ability to retain color and to form thin sheets, it is being used to make stationary folders, storage boxes, and the cube stickers for the Rubik's cubes. It is also used to construct trading card holders (such as baseball cards) with each sheet containing three or nine pockets for the trading cards. In medicine it is also used in hernia repair operations with a small sheet or film of PP placed over the spot of the hernia to prevent reformation of the surgical hernia.

Expanded polypropylene foam is used for radio-controlled model aircraft, automobiles, and trucks by hobbyists because of the ability of the foam to absorb impacts and its low density.

6.8 POLYMERS FROM 1,4-DIENES

6.8.1 INTRODUCTION

There are three important 1,4-dienes employed to produce commercially important polymers. These monomers possess a conjugated pi-bond sequence of $-C=C-C=C-$ that readily forms polymers with an average energy release of about 20 kcal/mol (80 kJ/mol) with the conversion of one of the double bonds into a lower (potential energy wise; generally more stable) energy single bond. For all of these products, cross-linking and grafting sites are available through the remaining double bond.

6.8.2 BUTADIENE RUBBER

1,4-Butadiene can form three repeat units as described in (6.37), the 1,2, *cis*-1,4, and *trans*-1,4. Commercial polybutadiene is mainly composed of the 1,4-*cis* isomer and is known as “**butadiene rubber**” (BR). In general, butadiene is polymerized using stereoregulating catalysts. The composition of the resulting polybutadiene is quite dependent on the nature of the catalyst such that almost total *trans*-1,4 units, or *cis*-1,4 units, or 1,2 units can be formed as well as almost any combination of these units. The most important single application of polybutadiene polymers is its use in automotive tires where over 10^7 tons are used yearly in the U.S. manufacture of automobile tires. BR is usually blended with natural rubber or *styrene-butadiene rubber* to improve tire tread performance, particularly wear resistance (Picture 6.10).

6.8.3 ABS

A second use of butadiene is in the manufacture of ABS copolymers where the stereogeometry is also important. A polybutadiene composition of about 60% *trans*-1,4, 20% *cis*-1,4, and 20% 1,2 configuration is generally employed in the production of ABS. The good low-temperature impact strength is achieved in part because of the low T_g values for the compositions. For instance, the T_g for *trans*-1,4-polybutadiene is about -14°C while the T_g for *cis*-1,4-polybutadiene is about -108°C . Most of the ABS rubber is made employing an emulsion process where the butadiene is initially polymerized forming submicron particles. The styrene-acrylonitrile copolymer is then grafted onto the outside of the BR rubber particles. ABS rubbers are generally tougher than *high-impact polystyrene* (HIPS) rubbers but are more difficult to process. ABS rubbers are used in a number of appliances including luggage, power tool housings, vacuum cleaner housings, toys, household piping, and automotive components such as interior trim.



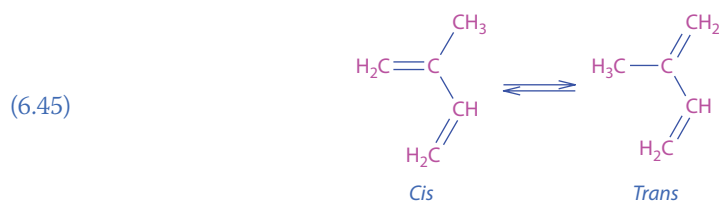
PICTURE 6.10 Over 50% of butadiene is used in tires.

6.8.4 HIGH-IMPACT POLYSTYRENE

Another major use of butadiene polymer is in the manufacture of **HIPS**. Most HIPS has about 4%–12% polybutadiene in it so that HIPS is mainly a polystyrene intense material. Here, the polybutadiene polymer is dissolved in a liquid along with styrene monomer. The polymerization process is unusual in that both a matrix composition of polystyrene and polybutadiene is formed and a graft between the growing polystyrene onto the polybutadiene is formed. The grafting provides the needed compatibility between the matrix phase and the rubber phase. The grafting is also important in determining the structure and size of rubber particles that are formed. The grafting reaction occurs primarily by hydrogen abstraction from the polybutadiene backbone either by growing polystyrene chains or alkoxy radicals if peroxide initiators are employed.

6.8.5 POLYISOPRENE

Interestingly, isoprene, 2-methyl-1,3-butadiene, exists as an equilibrium mixture of *cis*- and *trans*-isomers.



Polyisoprene is composed of four structures as shown in Equation 6.38. As in the case of polybutadiene, it is the *cis*-1,4 structure that is emphasized commercially. The *cis*-1,4-polyisoprene is similar to the *cis*-1,4-polybutadiene material except it is lighter in color, more uniform, and less expensive to process. Polyisoprene is composition-wise analogous to natural rubber. The complete *cis*-1,4 product has a T_g of about -71°C . Interestingly, isomer mixtures generally have higher T_g values. Thus, an equal molar product containing *cis*-1,4; *trans*-1,4; and 3,4 units has a T_g of about -40°C .

As with many polymers, polyisoprene exhibits non-Newtonian flow behavior at shear rates normally used for processing. The double bond can undergo most of the typical reactions such as carbene additions, hydrogenation, epoxidation, ozonolysis, hydrohalogenation, and halogenation. As with the case of the other 1,4-diene monomers, many copolymers are derived from polyisoprene or isoprene itself.

Polyisoprene rubbers are used in the construction of passenger, truck, and bus tires and inner liners as well as sealants and caulking compounds, sporting goods, gaskets, hoses, rubber sheeting, gloves, belts, and footwear.

6.8.6 POLYCHLOROPRENE

Polychloroprene was the first commercially successful synthetic elastomer and introduced in 1932 under the trade names DuPrene and Neoprene by DuPont. It was discovered by Carothers and coworkers. Because of its early discovery, good synthetic routes were worked out prior to the advent of good stereoregulating catalytic systems. Thus, polychloroprene is largely manufactured by emulsion polymerization using both batch and continuous systems. Free radical products contain mainly 1,4-*trans* units. Along with the four *main* structural units analogous to those of polyisoprene, sequence distributions are available for both polyisoprene and polychloroprene. Polymerization can occur with the growing end being the 4 end or the 1 end (Equation 6.46). Generally, the 1,4-polymerization sequence is favored with the growing end being carbon 4.



Structural regularity for inclusion of the 1,4-*trans* unit is inversely proportional to temperature. Thus, at 90°C the product contains about 85% of the *trans*-1,4 units while this increases to almost 100% at -150°C. Both uncured and cured (cross-linked) polychloroprene exists as largely crystalline materials because of the high degree of stereoregularity. Cured polychloroprene has good high tensile strength because of this and application of stress to the material, either before or after curing, increases the tensile strength. The *trans*-1,4-polychloroprene has a T_g of about -49°C while 1,4-*cis*-polychloroprene has a T_g of about -20°C.

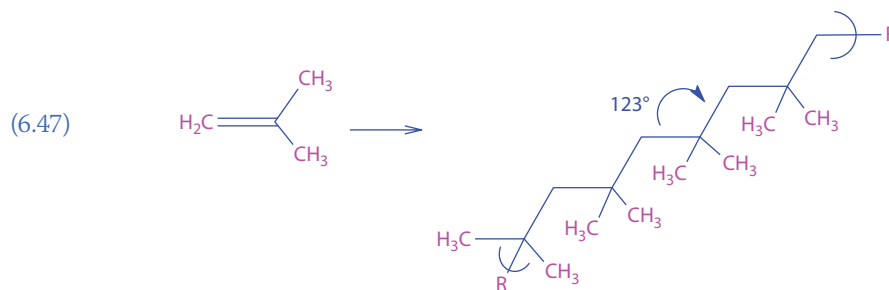
Compounding of polychloroprene is similar to that of natural rubber. Vulcanizing is achieved using a variety of agents including accelerators. Because of its durability, polychloroprene rubber is often used where deteriorating effects are present. It offers good resistance to oils, ozone, heat, oxygen, and flame (the latter because of the presence of the chlorine atom). Automotive uses include hoses, V-belts, and weather stripping. Rubber goods include gaskets, diaphragms, hoses, seals, conveyor belts, and gaskets. It is also used in construction for highway joint seals, bridge mounts and expansion joints, and soil-pipe gaskets. Further, it is used for wet-laminating and contact-bond adhesives, in coatings and dipped goods, as modifiers in elasticized bitumens and cements and in fiber binders.

As noted earlier, the presence of the chlorine atom in polychloroprene makes it less apt to burn in comparison to materials such as hydrocarbon-only elastomers. Thus, it is used in fire doors, some combat-related attire such as gloves and face masks and other similar applications. It is also used in the construction of objects that come into contact with water such as diving suits and fishing wader boots.

6.9 POLYISOBUTYLENE

Polyisobutylene (PIB), Equation 6.47, was initially synthesized in the 1920s but was later developed by William Sparks and Robert Thomas at Standard Oil's (to become Exxon) Linden, NJ laboratory. It is one of the few examples of the use of cationic catalysis to produce commercial

scale polymers. PIB and various copolymers are also called butyl rubber. Low-molecular-weight (about 5000 Da) PIB can be produced at room temperature but large chains (over 1,000,000 Da) are made at low temperatures where transfer reactions are suppressed.



Because of the symmetry of the monomer, it might be expected that the materials would be quite crystalline like linear PE. While PIB does crystallize under stress, it does not under nonstressed conditions. This is because the geminal dimethyl groups on alternating carbons in the backbone cause the bond angles to be distorted from about the usual tetrahedral bond angle of 109.5° to 123° forcing the chain to straighten out. As a consequence of this, the chains pack efficiently giving a relatively high-density material (density of 0.917 g/cm^3 compared to densities of about 0.85 g/cm^3 for many amorphous polymers) even when amorphous. This close packing reduces the incentive for crystallization, accounts for its low permeability, and produces an unusually low T_g of -60°C for such a dense material.

PIB is often produced as a copolymer containing a small amount (1%–10%) of isoprene. Thus, the random copolymer chain contains a low concentration of widely spaced isolated double bonds that are later cross-linked when the butyl rubber is cured.

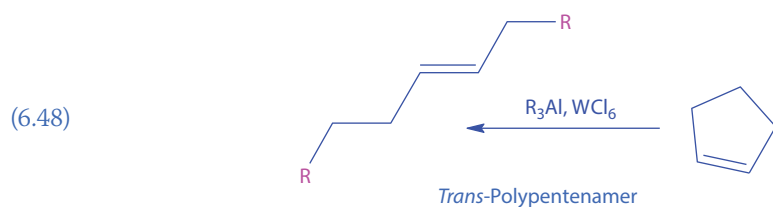
Butyl rubbers have lower permeability (including being essentially impermeable to air) and higher damping than most other elastomers making them ideal materials for tire inner liners, basketball inside coatings, and engine mounts. It is used as an adhesive, caulking compound, chewing gum base, and an oil additive. Its use as an oil additive is related to its change in shape with increasing temperature. Since lubricating oil is not a good solvent for PIB, which is present as a coil at room temperature. However, as the temperature increases, it begins to uncoil acting to counteract the decrease in viscosity of the oil as the temperature is increased. PIB is also used in sealing applications such as in roof repairs.

It is being used in a number of green chemistry applications. PIB (in the form of PIB succinimide) is added in small amounts to lubricating oils reducing the creation of an oil mist thus lowering the workers exposure to the oil mist. It is part of Elastol employed to clean up waterborne oil spills. It increases the crude oil's viscoelasticity resulting in an increased ability of the oil to remain together as it is vacuumed from the water's surface.

PIB acts as a detergent and is used as a fuel additive in diesel fuel reducing fuel injector fouling resulting in increased mileage and lowered unwanted emissions. It is also employed as part of a number of detergent packages that are blended into gasoline and diesel fuels.

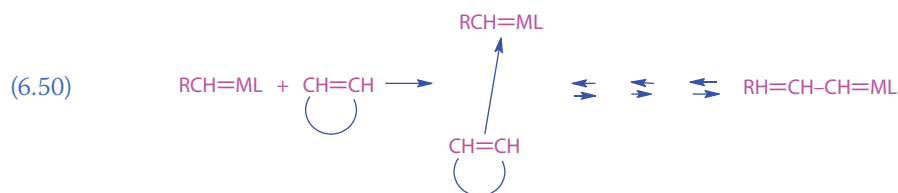
6.10 METATHESIS REACTIONS

Chauvin, Grubbs, and Schrock won the 2005 Nobel Prize for developing metathesis reactions. Olefin metathesis is a catalytically induced reaction wherein olefins, such as cyclobutene and cyclopentene, undergo bond reorganization resulting in the formation of so-called polyalkenamers. Because the resulting polymers contain double bonds that can be subsequently used to introduce cross-linking, these materials have been used to produce elastomeric materials as well as plastics. Transition metal catalysts are required for these reactions. Catalysts include typical Natta–Ziegler types and other similar catalysts–cocatalysts combinations. The reactions can be run at room temperature and the stereoregularity can be controlled through choice of reaction conditions and catalysts. For instance, the use of a molybdenum-based catalyst with cyclopentene gives the *cis* product whereas the use of a tungsten-based catalyst gives the *trans* product.



As expected, the metathesis polymerization of more strained cycloalkenes, such as cyclobutene, occurs more rapidly than less strained structures such as cyclopentene.

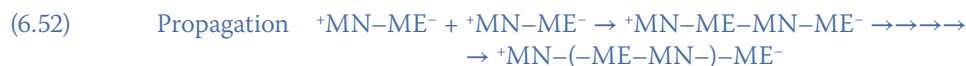
It is believed that polymerization occurs via a chain polymerization where ring opening occurs via complete scission of the carbon-carbon double bond through the reaction with metal carbene precursors giving an active carbene species (Equation 6.50).



where L is the ligand attached to the metal.

6.11 ZWITTERIONIC POLYMERIZATION

While most polymerizations require an initiator, catalyst or some other form of activation, zwitterionic copolymerizations do not. These copolymerizations require a specific combination of one monomer that is nucleophilic and a second that is electrophilic in nature. The interaction of these two comonomers gives a zwitterion that is responsible for both the initiation and propagation.



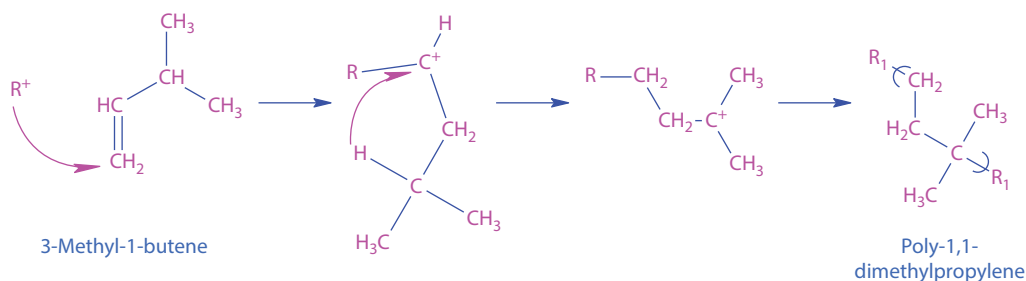
If growth involves only addition and condensation reactions, then an alternating copolymer is formed. Sometimes a lateral reaction occurs where the zwitterion interacts with one of the monomers giving a product that is a statistical copolymer.

6.12 ISOMERIZATION POLYMERIZATION

Isomerization polymerizations are polyaddition reactions where the propagating species rearranges to energetically preferred structures prior to subsequent chain growth.



In 1962 Kennedy reported the first isomerization polymerization using 3-methyl-1-butene to give a 1,1-dimethyl PP as follows:



(6.54)

Isomerization polymerizations can be associated with coordination catalyst systems, ionic catalyst systems, and free radical systems. The cationic isomerization polymerization of 4-methyl-1-pentene is of interest because the product can be viewed as an alternating copolymer of ethylene and isobutylene. This structure cannot be obtained by conventional approaches.

In the presence of certain ZNCs, an equilibrium exists between *cis*- and *trans*-1,3-pentadiene. Here, the *cis*-1,4-poly-pentadiene is formed from *trans*-1,3-pentadiene or from a mixture of the *cis* and *trans* isomers.

Such isomerizations are sometimes desired and sometimes are the cause of or explanation for unwanted structures. In the cationic polymerization forming poly(1-butene), nine different structural units have been found. Classical 1,2-hydride and 1,2-methide shifts, hydride transfer, and proton elimination account for these structures.

Unwanted branching of many polymers probably occurs through such isomerizations. PP, formed using cationic polymerization, has methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, gem-dimethyl, isobutyl, and *t*-butyl groups connected to the main chain.

6.13 PRECIPITATION POLYMERIZATION

Precipitation polymerization, also called slurry polymerization, is a variety of solution polymerization where the monomer is soluble but the polymer precipitates as a fine flock. The formation of olefin polymers via coordination polymerization occurs by a slurry process. Here, the catalyst is prepared and polymerization is carried out under pressure and at low temperatures, generally less than 100°C. The polymer forms a viscous slurry. Care is taken so that the polymer does not cake up on the sides and stirrer.

SUMMARY

1. Chain reactions, including ionic chain polymerization reactions, consist of at least three steps: initiation, propagation, and termination. Termination generally occurs through chain transfer producing a new ion and the *dead* polymer.
2. Cationic polymerizations occur with vinyl compounds that contain electron-donating groups using Lewis acids along with a cocatalyst as the initiators. Polymerizations generally occur at low temperatures in solvents with high dielectric constants. The DP is proportional to the concentration of monomer and overall rate of polymerization is proportional to the square of the monomer concentration. In general, the rate of polymerization is dependent on the dielectric constant of the solvent, resonance stability of the carbocation, the degree of solvation of the gegenion, and electropositivity of the initiator.
3. Monomers with electron-withdrawing groups can undergo anionic polymerization in the presence of anionic initiators. The rate of polymerization is dependent on the dielectric constant of the solvent, stability of the carbanion, electronegativity of the initiator, degree of solvation of the gegenion, and strength of the electron-withdrawing substituents.

4. Stereoregular polymers can be formed. These polymers can be divided into three general stereoregular unit combinations. When the pendent groups, such as methyl for PP, are all on one side of the polymer chain, the polymer combination is isotactic; when the methyl groups alternate from one side to the other, the polymer combination is syndiotactic; and when the position of the methyl group is somewhat random, it is atactic. The tacticity of polymers influences the physical properties of the products. In general, polymers with greater tacticity (order) have higher glass transition and melting temperatures, have a greater tendency to form crystalline products, are stronger, and are denser. Stereoregular polymers are produced at low temperatures in solvents that favor formation of ion pairs between the carbocation and the gegenion. One of the most widely used stereoregulating systems is called the Ziegler–Natta catalyst system that generally employs a transition metal salt such as titanium chloride and a cocatalyst such as alkylaluminum. A proposed mechanism involves a reaction on the surface of TiCl_3 , activated by the addition of an alkyl group from the cocatalyst. The monomer adds to this active site producing a pi-complex, which forms a new active center by insertion of the monomer between the titanium and carbon atoms. This step is repeated in the propagation reactions in which the alkyl group from the cocatalyst is the terminal group. Stereospecific polymers are also produced using the alfin and chromia on silica initiators. The alfin system consists of allyl sodium, sodium isopropoxide, and sodium chloride.
5. Soluble stereoregulating systems have been developed using an organometallic transition complex such as Cp_2TiCl_2 and a cocatalyst often MAO. This system has advantages over the Ziegler–Natta and similar systems in that the polymers produced are more stereoregular, a wider range of monomers can be used, and little or no catalyst incorporated into the polymers allowing the polymer to be directly used without having to undergo a procedure to remove catalyst.
6. Two of the highest volume polymers are made using ionic polymerization—HDPE and iPP. There exist a number of commercially available PEs that vary in extent and kind of branching, chain length, and amount of crystallinity.
7. A number of polymers have been made using ring-opening polymerizations. Nylon 6, similar to structure and properties to nylon 66, is made from the ring opening of the lactam caprolactam. PEO is made from the ring opening of ethylene oxide and is made more stable by capping the ends preventing ready depolymerization.

GLOSSARY

Alfin catalyst: Complex catalyst system consisting of allyl sodium, sodium isopropoxide, and sodium chloride.

Anionic polymerization: A polymerization initiated by an anion.

Butyl rubber (IIR): Copolymer of isobutylene and isoprene.

Capping: Reacting the end groups to produce a stable polymer.

Carbanion: Negatively charged organic ion.

Carbocation: Positively charged organic ion, that is, one lacking an electron pair on a carbon atom.

Cationic polymerization: Polymerization initiated by a cation and propagated by a carbonium ion.

Ceiling temperature: Threshold temperature above which a specific polymer is unstable and decomposes.

Celcon: Trade name of copolymer of formaldehyde and dioxolane.

Chain-reaction polymerization: A rapid polymerization based on initiation, propagation, and termination steps.

Chain transfer: Process in which a growing chain becomes a dead polymer by abstracting a group from some other compounds, thereby generating another active site.

Copolymer: Polymer chain composed of units from more than one monomer.

Copolymerization: Polymerization of a mixture of more than one monomer.

Coupling: Joining of two active species.

Gegenion: A counterion.

Initiation: Start of a polymerization.

Isomerization polymerization: Polyaddition reaction in which the propagation species rearranges to energetically preferred structures prior to chain growth.

Kraton: Trade name for an ABA block copolymer of styrene-butadiene-styrene.

Lactam: Heterocyclic amide with one nitrogen atom in the ring.

Leuchs' anhydride: Cyclic anhydride that decomposes to carbon dioxide and an amino acid.

Living polymers: Macroanions or macrocarbanions.

Macroions: Charged polymer molecules.

Metathesis reaction: Catalytically induced reaction wherein olefins undergo bond reorganization resulting in the formation of polyalkenamers.

Monadic: Polyamide produced from one reactant.

Natta, Giulio: One discoverer of stereospecific polymers.

Oxirane: Ethylene oxide.

Polyacetal: Polyoxymethylene.

Polychloral: Polymer of trichloroacetaldehyde.

Promoter: Strained cyclic ethers that are readily cleaved.

Propagation: Continuous successive chain extension in a chain reaction.

Soluble stereoregulating catalyst: Soluble catalysts requiring a metal active site, cocatalyst or counterion, and a ligand system; capable of producing polymers with high stereoregularity and a minimum of branching.

Termination: Destruction of active growing chain in a chain reaction.

Trioxane: Trimer of formaldehyde.

Ziegler, Karl: Discoverer of complex coordination catalysts.

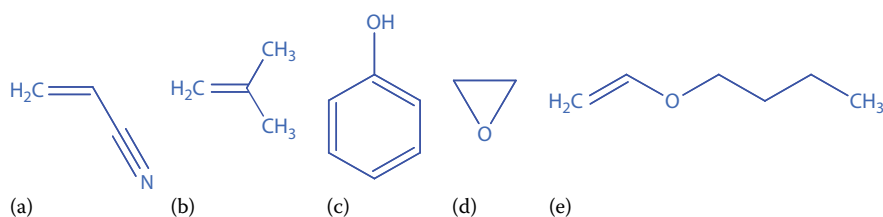
Ziegler–Natta (or Natta–Ziegler) catalyst: Able to produce stereoregular polymers.

Zwitterionic polymerization: Copolymerization between nucleophilic and electrophilic comonomers.

EXERCISES

- Describe the contents of the reaction flask 10 minutes after the polymerization of (a) reactants in a stepwise polymerization, such as dimethyl terephthalate and ethylene glycol, and (b) monomer in chain reactions, such as isobutylene.
- What is the initiator in the polymerization of isobutylene?
- What is the general name of the product produced by cationic initiation?
- What reactant besides the monomer is present in cationic chain propagation reactions?
- What name is used to describe the negatively charged counterion in cationic chain-reaction polymerizations?
- Is a Lewis acid (a) an electrophile or (b) a nucleophile?
- Is a Lewis base (a) an electrophile or (b) a nucleophile?
- Why isn't coupling a preferred termination step in the cationic chain polymerization of pure monomer?
- Is the usual configuration of polymers produced by ionic chain polymerization (a) head to tail or (b) head to head?
- Which condition would be more apt to produce stereoregular polymers in ionic chain polymerizations: (a) high temperatures or (b) low temperatures?
- Name (a) a thermoplastic, (b) an elastomer, and (c) a fiber that is produced commercially by ionic chain polymerization.
- Which technique would you choose for producing a polymer of isobutyl vinyl ether: (a) cationic or (b) anionic?
- Which technique would you choose for producing a polymer of acrylonitrile: (a) cationic or (b) anionic?
- Which of the following could be used to initiate the polymerization of isobutylene: (a) sulfuric acid, (b) boron trifluoride etherate, (c) water, or (d) butyllithium?

15. Which of the following could be polymerized by cationic chain polymerization?



16. Which polymer is more susceptible to oxidation: (a) HDPE or (b) PP?
17. When termination is by chain transfer, what is the relationship of average DP and the kinetic chain length?
18. What would be the composition of the product obtained by the cationic low-temperature polymerization of a solution of isobutylene in ethylene?
19. What is the relationship between the rate of initiation and the monomer concentration in ionic chain polymerization?
20. What effect will the use of a solvent with a higher dielectric constant have on the rate of propagation in ionic chain polymerization?
21. How does the rate constant k_p change as the yield of polymer increases?
22. Which will have the higher T_g value: (a) polystyrene or (b) polyisobutylene?
23. Which of the following could serve as an initiator for an anionic chain polymerization: (a) $\text{AlCl}_3\text{-H}_2\text{O}$, (b) $\text{BF}_3\text{-H}_2\text{O}$, (c) butyllithium, or (d) sodium metal?
24. What species, in addition to a dead polymer, is produced in a chain-transfer reaction with a macrocarbocation in cationic chain polymerization?
25. What is the relationship between R_i and R_t under steady-state conditions?
26. What is the relationship between average DP and R_p and R_i ?
27. Draw a structure of what iPP looks like.
28. What percentage of polymer is usually found when a polymer produced by chain-reaction polymerization is heated above its ceiling temperature?
29. What is the relationship between the average degree of polymerization and initiator concentration in cationic chain polymerization?
30. Can the polymers found in the bottom of a bottle of insolubilized formaldehyde solution be useful?
31. How would you prepare stable polymers from formaldehyde?
32. Why is the thermal decomposition of polymers of formaldehyde called unzipping?
33. Discuss advantages of the soluble stereoregulating catalysts in comparison to the Natta-Ziegler catalysts.
34. Why are there so many widely used polyethylenes?
35. How would you increase the flow rate of water in a fire hose?
36. Why is poly-3,3-bis(chloromethoxy)butylene crystalline?
37. Why are PP and PE the most widely used polymers?
38. What kind of polymers are made from lactones?
39. How could you remove unsaturated hydrocarbons from petroleum or coal tar distillates?
40. What species is produced by the reaction of an anionic chain polymerization initiator and the monomer?
41. What are the propagation species in anionic chain polymerizations?
42. Why are polymers produced by the anionic polymerization of pure monomers called *living polymers*?
43. Using the symbols A and B for repeating units in the polymer chain, which of the following is a block copolymer: (a) ABAABBABAAB, (b) ABABABABAB, or (c) AAAAAABBBBBB?
44. What is the most widely used monadic nylon?
45. What is the repeating unit for nylon-4?
46. What is the catalyst and cocatalyst in the most widely used Ziegler-Natta catalyst?
47. Name two structures that are possible from the polymerization of 1,3-butadiene.

48. What is the principal difference between propagation reactions with butyllithium and a Ziegler–Natta catalyst?
49. What are some physical properties that iPP would have in comparison to aPP?
50. Show the skeletal structures of *cis*- and *trans*-polyisoprene.
51. Write formulas for repeating units in the chains of (a) poly-1,4-isoprene and (b) poly-1,2-isoprene.
52. What is the most widely used catalyst for the production of HDPE?
53. What elastomer is produced by anionic chain polymerization?
54. What elastomer is produced by use of a Ziegler–Natta catalyst?
55. Why are there so many different kinds of PE?

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Free Radical Chain Polymerization (Addition Polymerization)

Since many synthetic plastics and elastomers and some fibers are prepared by free radical polymerization, this method is important. Table 7.1 contains a list of commercially important addition polymers including those that will be emphasized in this chapter because they are prepared using the free radical process.

As with other chain reactions, free radical polymerization is a rapid reaction that consists of the characteristic steps of initiation, propagation, and termination. Free radical initiators are produced by the homolytic cleavage of covalent bonds as well as numerous radiation-associated methods.

7.1 INITIATORS FOR FREE RADICAL CHAIN POLYMERIZATION

Free radical initiation can occur through application of heat (thermal), ultraviolet and visible light (photochemical), ionizing light, redox reagents, electricity (electrochemical), etc., that is, any process that creates the essential free radicals.

Light in the ultraviolet and visible range can disrupt selected bonds forming free radicals. Such disruption occurs as we are exposed to sunlight. Suntan treatments often contain certain compounds that can moderate this damaging radiation. Related compounds are also used in foods to give them longer shelf life. They are generally known as antioxidants. Synthetic antioxidants include benzophenones, benzils, and certain organic ketones. Thus, diphenylketone decomposes on exposure of ultraviolet radiation of the appropriate wavelength forming two free radicals (Equation 7.1).



The advantage of using such photochemical initiations is that polymerization can be carried out at room temperature.

When molecules are exposed to light of higher energy, shorter wavelength, or higher frequency, electrons can be removed or added depending on the specific conditions. Usual forms of ionizing radiation employed industrially and experimentally include neutrons, x-rays, protons, and alpha and beta particles. Oxidation-reduction, redox, reactions are also often employed to initiate free radical polymerizations in solution or heterogeneous organic-aqueous systems. Free radicals can be created by passing a current through a reaction system sufficient to initiate free radical polymerizations.

While application of heat or some other method can rupture the pi bond in the vinyl monomer causing the formation of a two-headed free radical that can act as a free radical initiator, peroxides and dinitriles are generally employed as initiators. This is a consequence of the general bond dissociation energy trend of $\text{C}-\text{H} > \text{C}-\text{C} > \text{C}-\text{N} > \text{O}-\text{O}$. Dinitrile or azo compounds such as AIBN require temperatures of about 70°C – 80°C to produce decomposition with free radical formation. Peroxides such as benzoyl peroxide (BPO) require temperatures in the range of 60°C – 140°C for decomposition and free radical formation. While the dissociation bond energy for $\text{C}-\text{N}$ is generally greater than for $\text{O}-\text{O}$, the formation of a stable N_2 molecule

TABLE 7.1 Industrially Important Addition Polymers

Polymer Name	Typical Properties	Typical Uses
Polyacrylonitrile	High strength; good stiffness; tough and abrasion resistant; good flex life; good resistance to moisture, stains, fungi, chemicals, and insects; good weatherability	Carpeting, sweaters, skirts, socks, slacks, baby garments
Poly(vinyl acetate)	Water sensitive with respect to physical properties such as adhesion and strength; good weatherability; fair adhesion	Lower mol. wt. used in chewing gum, intermediate in production of poly(vinyl alcohol); water-based emulsion paints
Poly(vinyl alcohol)	Water soluble; unstable in acid and base system; fair adhesion	Thickening agent for various suspension and emulsion systems; packaging film, wet-strength adhesive
Poly(vinyl butyral)	Good adhesion to glass; tough, good stability to sunlight; good clarity; insensitive to moisture	Automotive safety glass as the interlayer
Poly(vinyl chloride) and poly(vinylidene chloride); (called "the vinyls or vinyl resins")	Relatively unstable to heat and light; resistant to fire, insects, fungi, and moisture	Calendered products such as film, sheets, and floor coverings; shower curtains, food covers, rainwear, handbags, coated fabrics, and insulation for electrical cable and wire; old records
Polytetrafluoroethylene	Insoluble in most solvents, chemically inert, low dielectric loss, high dielectric strength, uniquely nonadhesive, low friction, constant electrical and mechanical properties from 20°C to 250°C; high impact strength	Coatings for frying pans, wire, and cable; insulation for motors, oils, transformers, and generators; gaskets; pump and valve packings; nonlubricated bearings; biomedical uses
Polyethylene (LDPE)	Good toughness and pliability over wide temp. range; outstanding electrical properties; good transparency in thin films; resistant to chemicals, acids, and bases; ages poorly in sunlight and oxygen; low density, flexible, resilient, high tear strength, and moisture resistant	Films, sheeting used as bags, textile materials, pouches, frozen foods, produce wrapping, etc.; drapes, table cloths, covers for ponds, greenhouses, trash can liners, etc.; electrical wire and cable insulator; coating for foils, papers, other films, and squeeze bottles
Polypropylene	Lightest major plastic; i-PP is major form sold; high tensile strength, stiffness, hardness, and resistance to marring; good gloss and high T_g allows it to be sterilized; good electrical properties, chemical inertness, and moisture resistance	Filament rope, webbing, cordage, carpeting, injection molding applications in appliances, small housewares, and automotive fields
Polyisoprene (<i>cis</i> -1,4-polyisoprene)	Structurally close to natural rubber; properties similar to those of natural rubber; good elasticity, rebound	Replacement of natural rubber; often preferred because of greater uniformity and cleanliness
SBR (styrene-butadiene rubber)	Random copolymer; generally slightly poorer physical properties than those of NR	Tire treads for cars; inferior to NR with respect to heat buildup and resilience, thus not used for truck tires; belting, molded goods, gum, flooring, rubber shoe soles, hoses, and electrical insulation
Butyl rubber (copolymer of isobutylene)	Amorphous isoprene, largely 1,4 isomer; good chemical inertness, low gas permeability, high viscoelastic response to stresses, and less sensitive to oxidative aging than most isoprene rubbers; better ozone stability than NR; good solvent resistance	About 60%–70% used for inner tubes for tires

(Continued)

TABLE 7.1 (Continued) Industrially Important Addition Polymers

Polymer Name	Typical Properties	Typical Uses
Polychloroprene (mostly 1,4 isomer)	Outstanding oil and chemical resistance; high tensile strength; outstanding resistance to oxidative degradation and aging; good ozone and weathering response; dynamic properties same or better than most synthetic rubbers	Can replace NR in most applications; gloves, coated fabrics, cable and wire coatings, hoses, belts, shoe heels, and solid tires
Polystyrene	Clear and easily colored; easily fabricated; transparent; fair mechanical and thermal properties; good resistance to acids, bases, and oxidizing and reducing agents; readily attacked by many organic solvents; good electrical insulation	Production of ion-exchange resins, heat- and impact-resistant copolymer, ABS, resins, etc.; foams, toys, plastic optical components, and lighting; fixtures, housewares, packaging, and home furnishings
Poly(methyl methacrylate)	Clear, transparent, colorless, good weatherability, good impact strength, resistant to dilute basic and acidic solutions; easily colored; good mechanical and thermal properties; good fabricability; poor abrasion resistance compared to glass	Used in cast sheets, rods, tubes, molding, extrusion compositions, tail- and signal-light lenses, dials, medallions, brush backs, jewelry, signs, lenses, and skylight "glass"; generally used where good light transmission is needed

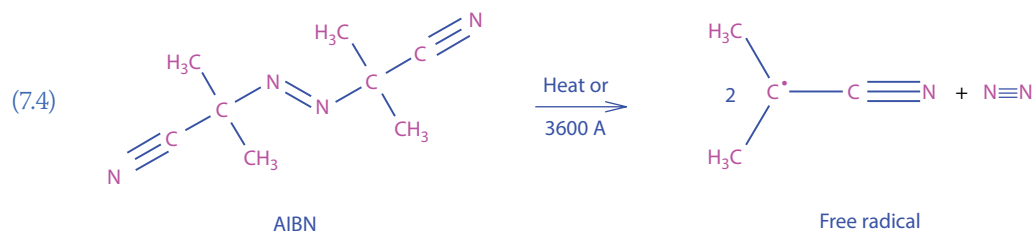
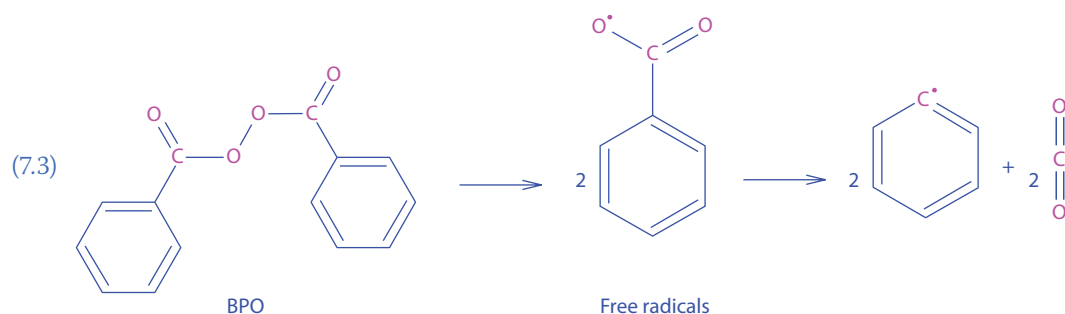
is the thermodynamic driving force due to an entropy effect allowing dissociation to occur at typically lower temperatures.

Here we will focus on the simple heat-induced decomposition of classical free radical initiators.

The rate of decomposition of initiators usually follows first-order kinetics and is dependent on the solvent present and the temperature of polymerization. The rate is usually expressed as a half-life time ($t_{1/2}$) where $t_{1/2} = \ln 2/k_d = 0.693/k_d$. The rate constant (k_d) changes with temperature in accordance with the Arrhenius equation:

$$(7.2) \quad k_d = A e^{-E_a/RT}$$

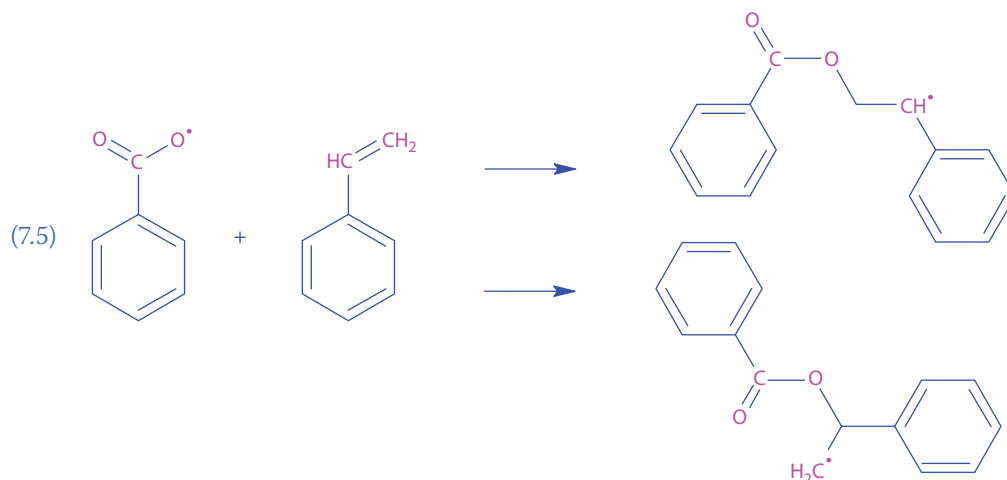
Typical equations for the dissociation of 2,2'-azobisisobutyronitrile (AIBN) and BPO are shown in (7.3) and (7.4). It should be pointed out that because of recombination, which is solvent dependent, and other side reactions of the created free radical (R^\bullet), the initiator efficiency is seldom 100%. Hence, an efficiency factor (f) is employed to show the fraction of effective free radicals produced.



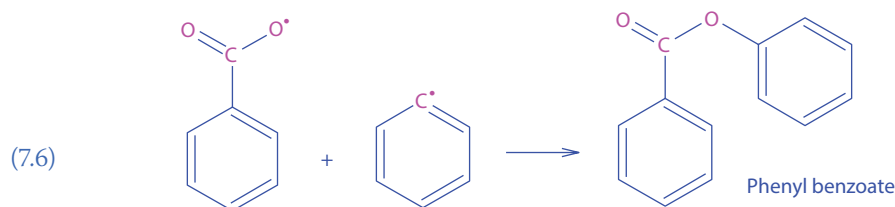
The precise structure of the initiating agent and initial addition to the monomer varies according to the reaction conditions, monomer, and initiator. For illustration, the peroxide bond in BPO breaks forming two benzoyl free radicals. A small portion of the benzoyl free radical decomposes into the phenyl radical as shown in (7.3).

The addition of a radical, formed from either monomer or initiator, to a vinyl monomer can occur in two ways. These are shown in (7.5) for the addition of the benzoyl radical to a styrene monomer. Addition can occur at the methylene not directly attached to the phenyl group as shown in (7.5, top) or it can add to the methylene directly attached to the phenyl group (7.5, bottom). Addition overwhelmingly occurs at the carbon not directly attached to the phenyl group since the unpaired electrons can take part in resonance with the phenyl group (7.5, top), whereas it does not occur for structure (7.5, bottom). Steric factors also favor this addition. This is also responsible for the greatly favored formation of the head-to-tail polymer chain structure.

For styrene, the major reaction (7.5, top) involves direct addition of the benzoyl radical to the tail end of the styrene monomer creating a molecule where the radical resides at the head or more sterically demanding and more radical stabilizing site.



The BPO decomposes with a specific rate constant of about 10^{-8} s^{-1} ; an Arrhenius constant, A , of about 10^{16} ; and an activation energy of about 28 kcal/mol (about 115 kJ/mol). As noted before, not all radicals initiate new chains. Some terminate prior to initiation forming inactive products mainly phenyl benzoate (7.6). Thus, an efficiency constant, f , is used that reflects the ratio of BPO that actually forms chains.



While initiation can occur via a number of routes, as noted before, we will emphasize the use of chemical initiators for the formation of the free radicals necessary to begin the free radical polymerization process.

7.2 MECHANISM FOR FREE RADICAL CHAIN POLYMERIZATION

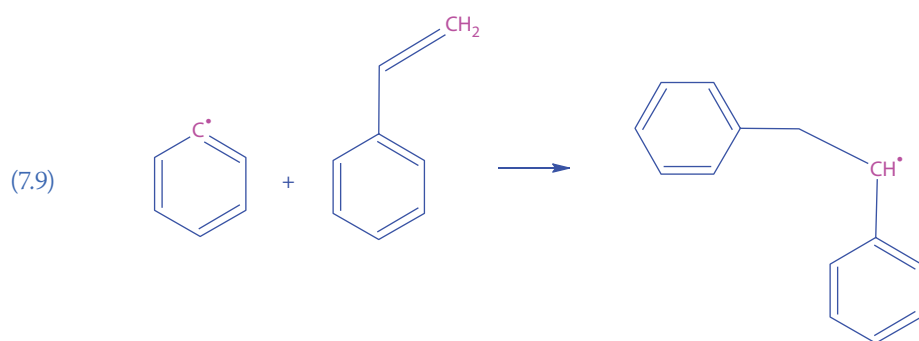
In general, the decomposition of the initiator (I) may be expressed by the following equation in which k_d is the specific rate or decay constant:



$$(7.8) \quad R_d = -\frac{d[I]}{dt} = k_d[I]$$

where R_d is the rate of decomposition.

Initiation of a free radical chain takes place by addition of a free radical (R^\bullet) to a vinyl monomer (Equation 7.9). Polystyrene (PS) will be used to illustrate the typical reaction sequences. (Styrene, like many aromatic compounds, is toxic and concentrations that come into contact with us should be severely limited.) For the initiator BPO, the initiator can be any of several radicals derived from its decomposition. The most frequent (about 80%) initiator is the benzoyl radical as shown in (7.5, top). Another initiator is the phenyl radical as shown in (7.9). Both initiators lead to the formation of essentially the same PS, differing only in the precise identity of the end group. It is important to note that the free radical (R^\bullet) is a companion of all polymerizing species and is part of the polymer chain acting as an end group and hence should not be called a catalyst even though it is often referred to as such.



$$(7.11) \quad R_i = \frac{d[RM^\bullet]}{dt} = k_i[R^\bullet][M]$$

where

R_i is the rate of initiation

R^\bullet is the free radical from BPO

The rate of decomposition of the initiator (I) (Equation 7.7) is the rate-controlling step in the free radical polymerization as well as formation of growing chains. Thus, the overall expression describing the rate of initiation can be given as

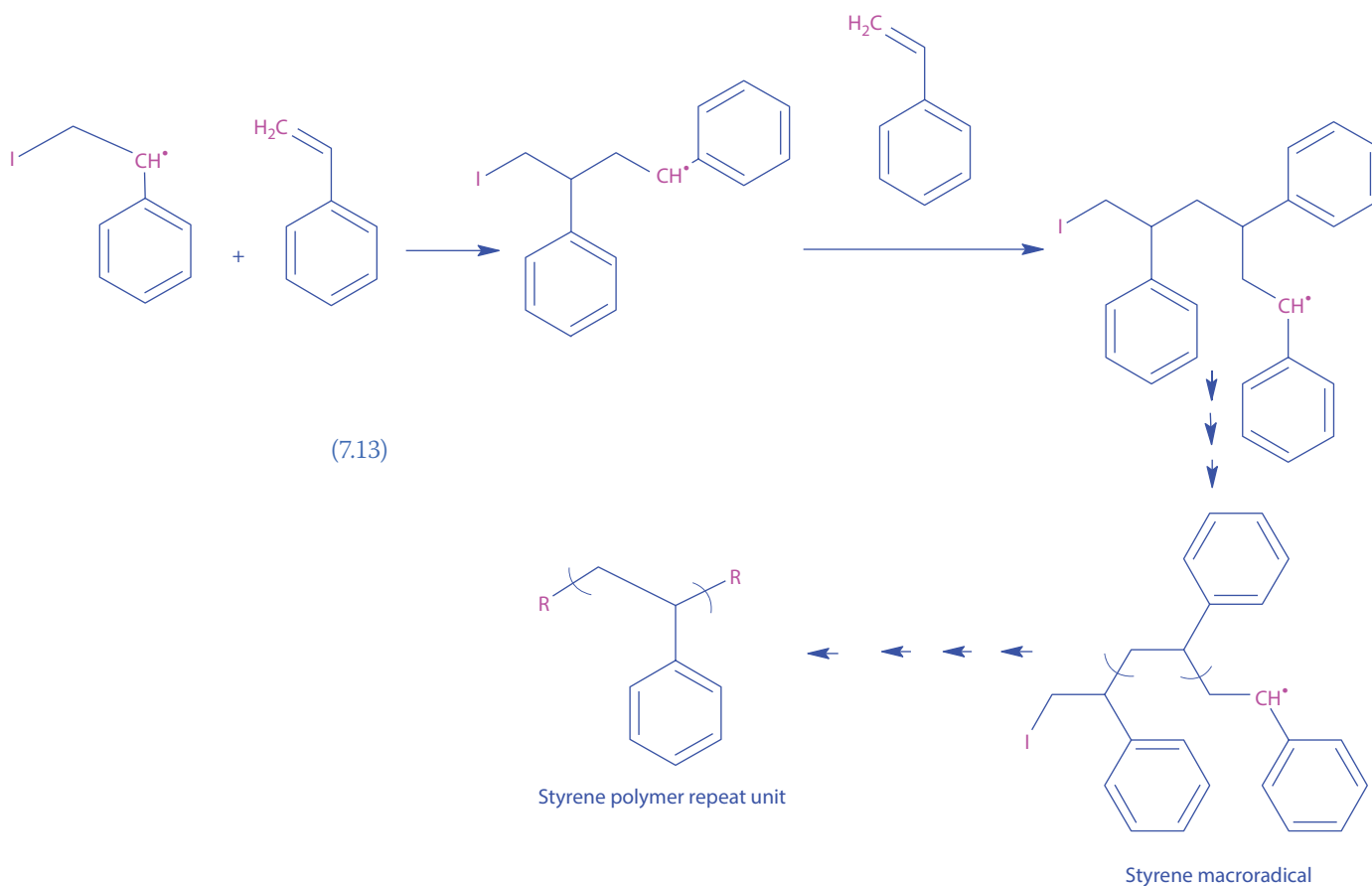
$$(7.12) \quad R_i = 2k_d f[I]$$

where “ f ” is the efficiency factor and is a measure of the fraction of initiator radicals that produce growing radical chains, that is, they are able to react with monomer.

A “2” is inserted in Equation 7.12 because, in this presentation, for each initiator molecule that decomposes, two radicals are formed. The “2” is omitted from Equation 7.7 because this rate expression describes the rate of decomposition of the initiator but not the rate of formation of free radicals R^\bullet . (Similarly, in Equations 7.18 and 7.20, each termination results in the loss of two growing chains, thus a “2” appears in the descriptions.)

Propagation is a bimolecular reaction (Equation 7.13), which takes place by the addition of a new free radical (RM^\bullet) to another molecule of monomer (M), and by many repetitions of this step. While there may be slight changes in the propagation rate constant (k_p) in the first few steps, the rate constant is generally considered to be independent of chain length. This is what is also

experimentally found. Hence, the symbols M^\bullet , RM^\bullet , and RM_nM^\bullet may be considered equivalent in rate equations for free radical polymerization.



Since the specific rate constants are approximately independent of the length of the growing chain, one specific rate constant is used to represent all of the propagation steps, k_p .

The rate of demise of monomer with time is described as

$$(7.14) \quad -\frac{d[M]}{dt} = k_p[M^\bullet][M] + k_i[R^\bullet][M]$$

that is, monomer consumption only occurs in reactions described by Equations 7.9 and 7.13.

For long chains, the consumption of monomer by the initiation step (Equation 7.13) is small and can be neglected allowing Equation 7.14 to be rewritten as

$$(7.15) \quad R_p = -\frac{d[M]}{dt} = k_p[M^\bullet][M]$$

The polarity of the functional group in the monomers polymerized by free radical chain polymerization is between the positively inclined monomers characterized by undergoing cationic polymerization and the negatively inclined monomers characterized by undergoing anionic polymerization. Figure 7.1 contains a listing of the addition polymerization routes taken by various monomers. As is true for the configuration of ionic growing chains, free radical polymers are also formed so that addition gives a head-to-tail configuration. This is because functional groups on the vinyl monomers are better at stabilizing the radical than is the hydrogen atom and because this balances the steric requirements present as addition occurs.

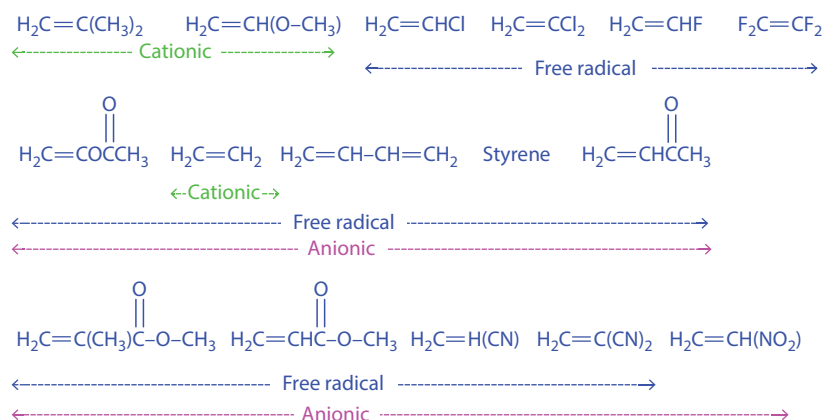
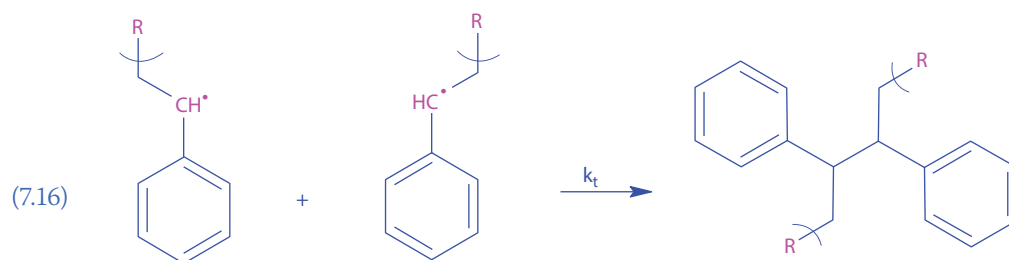


FIGURE 7.1 Type of chain initiation for some common monomers in order of general decrease in electron density associated with the double bond and their tendency to undergo chain polymerization.

Unlike ionic polymerizations, the termination of the growing free radical chains usually occurs by coupling of two macroradicals. Thus, the kinetic chain length (ν) is equal to $\text{DP}/2$. The chemical and kinetic equations for bimolecular termination are shown here:

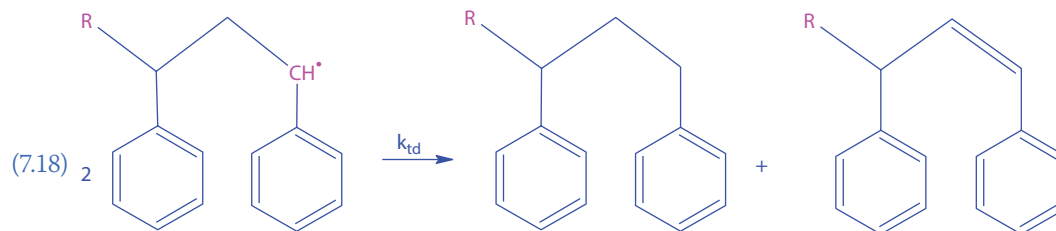


Termination is a head-to-head configuration at the juncture of the two macroradicals. The extent of coupling termination can then be obtained by determining the extent of head-to-head configuration in the product. The following is the kinetic equation for coupling termination:

(7.17)

$$R_t = -\frac{d[\text{M}^*]}{dt} = 2k_t[\text{M}^*][\text{M}] = 2k_t[\text{M}^*]^2$$

In some situations, termination occurs by disproportionation. This termination process involves chain transfer to a hydrogen atom from one chain end to the free radical chain end of another growing chain, resulting in one of the “dead” polymer chains having an unsaturated chain end.



(7.19)

$$R_{td} = 2k_{td}[\text{M}^*]^2$$

The kinetic chain length for termination by disproportionation is $\overline{DP} = v$ (compared with the relationship for coupling of $\overline{DP} = 2v$, the extent of the two types of termination is experimentally found by determining the number of head-to-head sites and unsaturated end groups).

While styrene macroradicals typically terminate by coupling, methyl methacrylate macroradicals terminate by coupling at temperatures below 60°C but by disproportionation at higher temperatures.

The kinetic chain length is described in the following equation:

$$(7.20) \quad v = \frac{R_p}{R_i} = \frac{R_p}{R_{td}} = \frac{k_p[M][M^*]}{2k_{td}[M^*]^2} = \frac{k_p[M]}{k_{td}[M^*]} = \frac{k'[M]}{[M^*]}$$

Because it is experimentally found that the number of growing chains is constant, there exists a steady state in M^* so that $R_i = R_{td}$. (A similar scenario can be used to develop rate expressions for coupling.)

While equations such as (7.15), (7.17), (7.19), and (7.20) are theoretically important, they contain $[M^*]$ that is difficult to experimentally determine and are thus practically of little use. The following is an approach to render such equations more useful by generating a description of $[M^*]$ that involves more easily experimentally accessible terms.

The rate of monomer-radical *change* is described by

$$(7.21) \quad \frac{d[M^*]}{dt} = [\text{monomer-radical formed}] - [\text{monomer-radical utilized}] = k_i[R^*][M] - 2k_t[M^*]^2$$

As noted before, it is experimentally found that the number of growing chains is approximately constant over a large extent of reaction. This situation is referred to as a “steady state.” For Equation 7.21, this results in $d[M^*]/dt = 0$ and

$$(7.22) \quad k_i[R^*][M] = 2k_t[M^*]^2$$

Additionally, a steady state value for the concentration of R^* exists giving

$$(7.23) \quad \frac{d[R^*]}{dt} = 2k_d f[I] - k_i[R^*][M] = 0$$

Solving for $[M^*]$ from Equation 7.22 gives

$$(7.24) \quad [M^*] = \left(\frac{k_i[R^*][M]}{2k_t} \right)^{1/2}$$

and $[R^*]$ from Equation 7.23 gives

$$(7.25) \quad [R^*] = \frac{2k_d f[I]}{k_i[M]}$$

Substitution into Equation 7.24 the expression for $[R^*]$, we obtain an expression for $[M^*]$ that contains somewhat easily experimentally determinable terms:

$$(7.26) \quad [M^*] = \left(\frac{k_d f[I]}{k_t} \right)^{1/2}$$

Using this relationship for $[M^*]$, we get more useful rate (Equation 7.27) and kinetic chain length (7.29) equations:

$$(7.27) \quad R_p = k_p[M][M^*] = k_p[M] \left(\frac{k_d f[I]}{k_t} \right)^{1/2} = \left(\frac{k_p^2 k_d f}{k_t} \right)^{1/2} [M][I]^{1/2} = k''[M][I]^{1/2}$$

Thus, the rate of propagation, or polymerization, is directly proportional to the concentration of the monomer and square root concentration of initiator.

In preparation of describing the kinetic chain length, we can also describe the rate of termination using the new description for $[M^*]$:

$$(7.28) \quad R_t = 2k_t[M^*]^2 = \frac{2k_t k_d f[I]}{k_t} = 2k_d f[I]$$

$$(7.29) \quad \overline{DP} = \frac{R_p}{R_i} = k_p[M] \left(\frac{(k_d f[I]/k_t)^{1/2}}{2k_t f[I]} \right) = \frac{k_p[M]}{2(k_d k_t f[I])^{1/2}} = \frac{k'_p[M]}{[I]^{1/2}}$$

Thus, chain length is directly proportional to monomer concentration and inversely proportional to the square root of initiator concentration.

Typical energies of activation for propagation and termination are given in Table 7.2 and typical free radical kinetic values in Table 7.3.

As done in Chapter 6, the effect of temperature can be determined using average activation of the various steps. Again, the rates of all single step reactions increase as the temperature increases, but the overall result may be different for complex reactions. For free radical polymerizations, the activation energies are generally of the order $E_d > E_i = E_p > E_t$. Remembering that the description of the specific rate constant is

$$(7.30) \quad k = A e^{-E_a/RT}$$

The overall or “net” activation energy is

$$(7.31) \quad E_{(\text{overall})} = E_t + E_i + E_p + E_d$$

Using only the specific rate constants involved with propagation from Equation 7.27, we have

$$(7.32) \quad R_p \propto k_p^2 k_d / k_t$$

TABLE 7.2 Energies of Activation for Propagation (E_p) and Termination (E_t) in Free Radical Chain Polymerization

Monomer	E_p (kJ/mol)	E_t (kJ/mol)
Methyl acrylate	30	22
Acrylonitrile	17	23
Butadiene	39	—
Ethylene	34	—
Methyl methacrylate	26	12
Styrene	33	12
Vinyl acetate	31	22
Vinyl chloride	15	18

TABLE 7.3 Typical Free Radical Kinetic Values

Specific Rate Constant		Activation Energies (kJ/mol)	
k_d	10^{-3} s^{-1}	E_d	80–160
k_i	10^3 L/mol-s	E_i	20–30
k_p	10^3 L/mol-s	E_p	20–40
k_t	10^7 L/mol-s	E_t	0–20

so that the overall activation energy using average values is a positive value (Equation 7.33) so the overall rate of polymerization increases as temperature increases.

$$(7.33) \quad E_{p(\text{overall})} \propto 2E_p + E_d - E_t = 2 \times 30 + 120 - 10 = 170$$

For chain length, from Equation 7.29 we have

$$(7.34) \quad \overline{DP} \propto \frac{k_p}{2k_d k_t}$$

so that the overall activation energy using average values is

$$(7.35) \quad \overline{DP}(\text{overall}) \propto E_p - E_d - E_t = 30 - 120 - 10 = -100$$

so that \overline{DP} decreases as temperature increases as pictured in Figure 5.4.

The Gibbs free energy relationship for a reversible process at constant temperature for polymerization is described by

$$(7.36) \quad \Delta G_p = \Delta H_p - T\Delta S_p$$

where ΔH_p is the heat of polymerization defined by

$$(7.37) \quad \Delta H_p = E_p - E_{dp}$$

where E_p is the activation energy for propagation and E_{dp} is the activation energy for depolymerization.

The entropy term is negative so that it is the enthalpy or energy term that “drives” the polymerization. At low temperatures, the enthalpy term is larger than the $T\Delta S_p$ term so that polymer growth occurs. At some temperature, called the “ceiling temperature,” the enthalpy term and entropy term are the same and $\Delta G_p = 0$. Above this temperature, depolymerization occurs more rapidly than polymer formation so that polymer formation does not occur. At the ceiling temperature, depolymerization and polymerization rates are equal. The ceiling temperature is then defined as

$$(7.38) \quad T_c = \frac{\Delta H_p}{\Delta S_p}$$

since $\Delta G_p = 0$.

The ceiling temperature for styrene is about 310°C, for ethylene it is 400°C, for propylene it is 300°C, for methyl methacrylate it is 220°C, for tetrafluoroethylene it is 580°C, and for alpha-methylstyrene it is only 61°C.

It is interesting to note that due to their industrial importance, free radical polymerizations are the most studied reactions in chemistry. Furthermore, the kinetic approaches taken in this chapter are experimentally verified for essentially all typical free radical vinyl polymerizations.

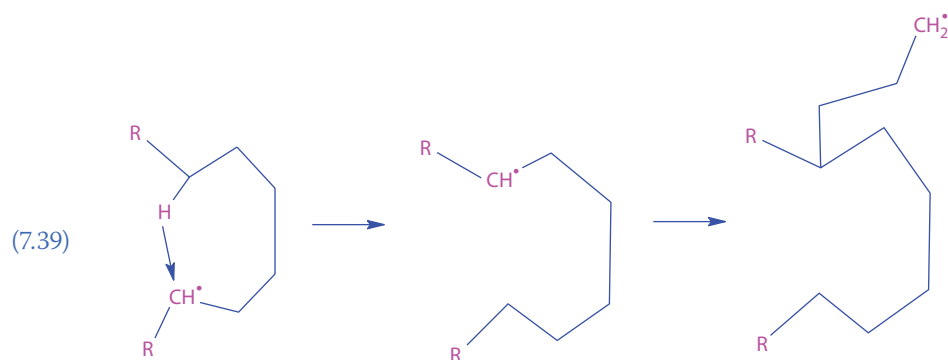
There is some tendency for the formation of stereoregular sequences, particularly at low temperatures, but ionic and coordination catalysts are far superior in this aspect and are used to create stereoregular macromolecules.

Several additional comments are appropriate concerning chain type polymerization and termination. First, since the slow step is the initiation step and the other steps, and especially termination, have very low energy of activations and so are very fast, how does polymer form? Consider the relative concentrations of the various species. The concentration of polymer monomer is very high relative to the concentration of the free radical species favoring the formation of chain growth. The rate of termination is proportional to the square of the concentration of growing chain for both coupling (7.18) and disproportionation (7.20) and as a consequence of the concentration of growing chain being relatively quite small, polymer is allowed to form. Thus, chain

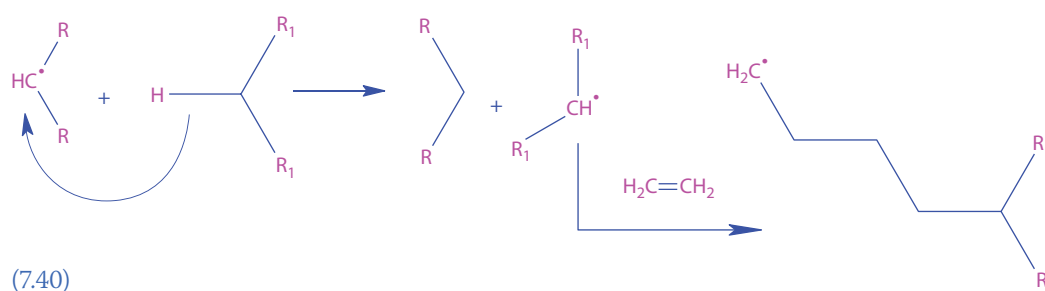
growth resulting in polymer formation is the consequence of the high concentration of monomer and low concentration of growing chains. Second, in general as the steric hindrance increases, the tendency for termination occurring through disproportionation increases since coupling requires the approach of the ends of two growing chains. This approach of growing chain ends becomes, in general, less favorable as the steric hindrance increases.

7.3 CHAIN TRANSFER

Transfer of the free radical to another molecule serves as one of the termination steps for general polymer growth. Thus, transfer of a hydrogen atom at one end of the chain to a free radical end of another chain is a chain transfer process we dealt with in Section 7.2 under termination via disproportionation. When abstraction occurs intramolecularly or intermolecularly by a hydrogen some distance from the chain end, branching results. Each chain transfer process causes the termination of one macroradical and produces another macroradical. The new radical sites serve as branch points for chain extension or branching. As noted earlier, such chain transfer can occur within the same chain as shown here:



Chain transfer can also occur between chains:



Chain transfer can also occur with initiator, impurity, solvent, or other additive present in the polymerization system. While the average chain length is equal to R_p divided by the sum of all termination reactions, it is customary to control all termination steps except the one that is being studied. Chain transfer to all other molecules, except solvent or some special additive, is typically negligible.

The chain transfer reaction decreases the average chain length. This decrease in chain length increases as the concentration of the chain transfer agent (S) increases and as the tendency of the chain transfer agent to “chain transfer” is increased. The resulting degree of polymerization (DP) is equal to that which would have been obtained without the solvent or additive plus a factor related to the product of the ratio of the rate of propagation (R_p) and the rate of chain transfer (R_{tr}) and the ratio of the concentration of the monomer [M] to the concentration of chain transfer agent [S].

The Mayo equation, Equation 7.41, that gives positive slopes when the data are plotted, is the reciprocal relationship derived from the previously cited expression. The ratio of the rate of cessation or termination by transfer to the rate of propagation is called the chain transfer constant (C_s):

$$(7.41) \quad \frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_s \frac{[S]}{[M]}$$

The chain transfer constant is given as

$$(7.42) \quad C_s = \frac{k_{tr}}{k_p}$$

As shown in Figure 7.2, the molecular weight of PS is reduced when it is polymerized in solvents, and the reduction or increase in slope is related to the chain transfer efficiency of the solvent. The slopes in this figure are equal to C_s .

Chain transfer constants of various solvents, including those given in Figure 7.2, are given in Table 7.4.

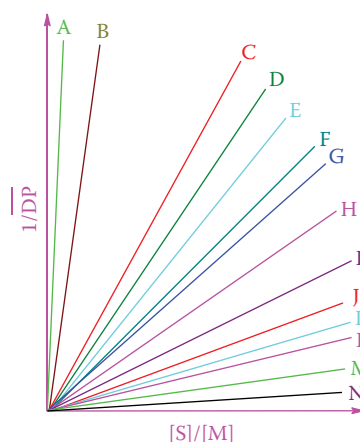


FIGURE 7.2 Molecular weight of polystyrene as a function of solvent and solvent concentration: A = *n*-butylmercaptan, B = carbon tetrabromide, C = carbon tetrachloride, D = *o*-cresol, E = *p*-cresol, F = *m*-cresol, G = phenol, H = sec-butylbenzene, I = cumene, J = ethylbenzene, K = chloroform, L = *n*-heptane, M = toluene, and N = benzene where [S] is the concentration of chain transfer agent and [M] is the concentration of styrene monomer.

TABLE 7.4 Chain Transfer Constants of Solvent to Styrene in Free Radical Chain Polymerization at 60°C

Transfer agent	$C_s \times 10^4$	Transfer agent	$C_s \times 10^4$
Acetic acid	2.0	1-Dodecanethiol	148,000
Benzene	0.01	Hexane	0.9
Butyl alcohol	0.06	<i>N,N</i> -Dimethylaniline	12
<i>t</i> -Butyl alcohol	6.7	1-Naphthalenethiol	1500
Butyl disulfide	0.24	1-Octanethiol	190,000
Carbon tetrabromide	18,000	<i>p</i> -Methoxyphenol	260
Carbon tetrachloride	84	Phenol	8.1
Chloroform	0.5	Triethylamine	1.4
<i>o</i> -Chlorophenol	6.0	Toluene	0.105
2,6-Ditert-butylphenol	49	Water	0

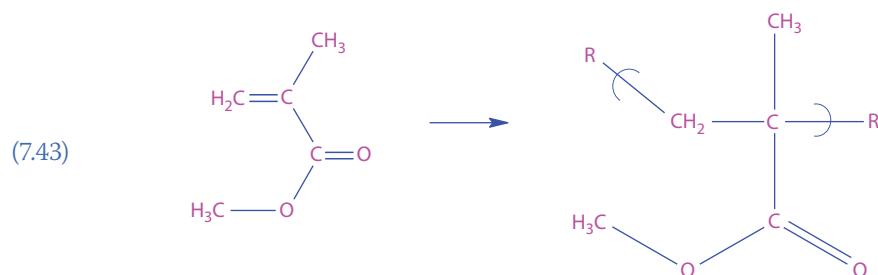
Chain transfer agents have been called regulators (of molecular weight). When used in large proportions, they are called telogens, since they produce low-molecular-weight polymers (telomers).

7.4 POLYMERIZATION TECHNIQUES

The principal free radical polymerization techniques are bulk, solution, and emulsion. Tables 7.5 and 7.6 briefly describe these techniques.

7.4.1 BULK POLYMERIZATION

Bulk polymerization of a liquid monomer such as methyl methacrylate is relatively simple in the absence of oxygen where small bottles or test tubes are used as the reaction vessel. The monomer can be heated in the presence of an initiator giving a clear plastic shaped like the container, but a little smaller because of shrinkage. The volume of the monomers is generally larger than the final polymers, thus, the density of the polymer is greater than that of the original monomer. Poly(methyl methacrylate) (PMMA) (7.43) is sold under the trade names Lucite and Plexiglass as an atactic amorphous polymer.



Polymers such as the methacrylates play an essential role as photoresists. To make a photoresist, the methacrylate polymer is deposited onto silicon dioxide. A mask, which shields specific regions from subsequent exposure to light, is placed over the methacrylate polymer resist. The combination is exposed to light of such strength as to induce methacrylate polymer bond breakage producing a somewhat degraded methacrylate product that is more soluble in organic liquids allowing the preferential removal of the exposed photoresist. These methacrylate polymers are especially designed to allow both easy degradation and subsequent easy removal. One of these is a copolymer with adamantane and lactone-containing units (7.44).

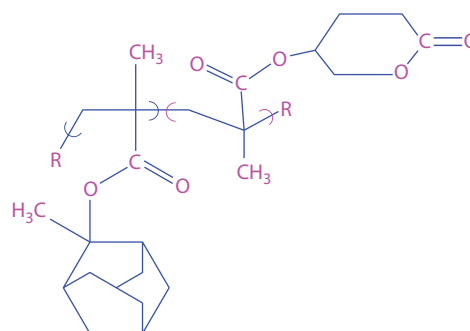
TABLE 7.5 Types of Polymerization Systems

Monomer–Polymer Phase Relationship	Monomer Location	
	Continuous	Dispersed
Homogeneous (same phase)	Bulk, solid-state, solution	Suspension
Heterogeneous (different phase)	Bulk with polymer precipitating	Emulsion; suspension with polymer precipitating

TABLE 7.6 Summary of Popular Polymerization Techniques

Bulk	Simplest of the techniques requiring only monomer and monomer-soluble initiator, and perhaps a chain transfer agent for molecular weight control. Characterized, on the positive side, by high polymer yield per volume of reaction and easy polymer recovery. Difficulty of removing unreacted monomer and heat control are negative features. Examples of polymers produced by bulk polymerization include poly(methyl methacrylate), polystyrene, and low-density (high pressure) polyethylene.
Solution	Monomer and initiator must be soluble in the liquid and the solvent must have the desired chain transfer characteristics, boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). The presence of the solvent assists in heat removal and control (as it also does for suspension and emulsion polymerization systems). Polymer yield per reaction volume is lower than for bulk reactions. Also, solvent recovery and removal (from the polymer) is necessary. Many free radical and ionic polymerizations are carried out utilizing solution polymerization including water-soluble polymers prepared in aqueous solution (namely), poly(acrylic acid), polyacrylamide, and poly(<i>N</i> -vinylpyrrolidinone). Polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polybutadiene are prepared from organic solution polymerizations.
Suspension	A water-insoluble monomer and initiator are used. Again, a chain transfer agent may be used to control chain size. Stirring is usual. Droplets of monomer-containing initiator and chain transfer agent are formed. A protective colloidal agent, often poly(vinyl alcohol), is added to prevent coalescence of the droplets. Near the end, the particles become hard and are recovered by filtration. Because the liquid is water based, solvent recovery and treatment problems are minimal. The products may contain a number of impurities including any of the agents added to assist in the polymerization process. Polymers produced by suspension polymerization include poly(vinyl chloride), polystyrene resins, and copolymers such as poly(styrene- <i>co</i> -acrylonitrile), SAN, and poly(vinyl chloride- <i>co</i> -vinylidene chloride).
Emulsion	The system usually contains a water-soluble initiator (in contrast to the requirement that the initiator must not be water soluble in suspension polymerizations), chain transfer agent, and a surfactant. The hydrophobic monomer forms large droplets that are stabilized by the surfactant. At a certain surfactant concentration, the surfactant molecules form micelles that contain 50–100 surfactant molecules. During the polymerization, the monomer, which has a small but real water solubility, migrates from the monomer droplets through the water and into these micelles. Polymerization begins when the water-soluble initiator enters into the monomer-containing micelle. Because the concentration of micelles (about $10^{21}/\text{L}$) is high compared with the concentration of monomer droplets (about $10^{13}/\text{L}$), the initiator is more likely to enter a micelle than a monomer droplet. As polymerization continues, monomer is transferred to the growing micelles. At about 50%–80% conversion, the monomer droplets disappear and the micelles become large polymer-containing droplets. This suspension is called a latex. The latex is stable and can be used as is or the polymer recovered by coagulation. In inverse emulsion polymerization, the monomer, which is hydrophilic, is dispersed in an organic liquid. Here, the monomer is usually contained in an aqueous solution.

(7.44)



Modified methacrylate copolymer

This type of photoresist is called a “positive photoresist” since it is the exposed area that is removed.

Negative photoresists are formed from polymers that undergo reactions that decrease their solubility when exposed to radiation. Thus, polymers such as *cis*-1,4-polyisoprene (7.45) cross-link when exposed to the appropriate radiation giving insoluble products.



The rate of bulk polymerization can be followed by monitoring the change in volume or increase in viscosity. When the viscosity is high, the termination reaction is hindered since the macroradicals are unable to diffuse readily in the viscous medium. Thus, the number of growing chains increases. This autoacceleration, called the Norrish–Trommsdorff, Trommsdorff, or gel effect, causes the formation of unusually high-molecular-weight chains. Since vinyl polymerizations are exothermic, there is a buildup of heat that further causes an additional autoacceleration of the reaction. If the temperature buildup is not controlled, it is possible that an explosion will occur. While the temperature can be easily controlled within a small test tube, it is more difficult in a large batch process. Stirring and external cooling are employed to control the polymerization process.

7.4.2 SUSPENSION POLYMERIZATION

Water-insoluble monomers such as vinyl chloride may be polymerized as suspended droplets (10–1000 nm in diameter) in a process called suspension (pearl) polymerization. Coalescence of droplets is prevented by the use of small amounts of water-soluble polymers, such as poly(vinyl alcohol) (PVA). The suspension process is characterized by good heat control and ease of removal of the discrete polymer particles.

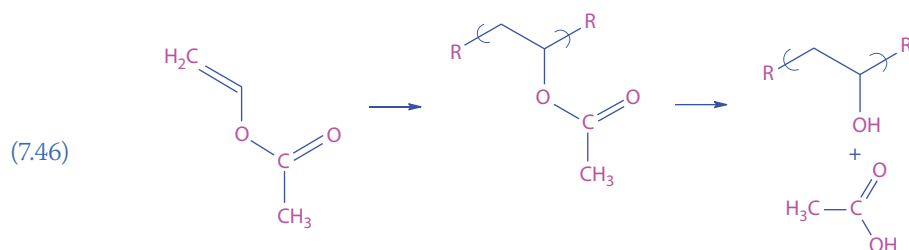
Since poly(vinyl chloride) (PVC) is insoluble in its monomer, it precipitates as formed in the droplet. This is actually advantageous, since it permits ready removal of any residual carcinogenic monomer from the solid beads by stripping under reduced pressure.

7.4.3 SOLUTION POLYMERIZATION

Monomers may also be polymerized in solution using good or poor solvents for homogeneous and heterogeneous systems, respectively. In solution polymerizations, solvents with low-chain-transfer constants are used to minimize reduction in chain length.

Poly(vinyl acetate) (PVAc) may be produced by the polymerization of vinyl acetate (7.46). The viscosity of the solution continues to increase until the reaction is complete. Dilute polymer solutions are used to prevent the onset of autoacceleration because of the gel effect.

PVAc is used in adhesives and coatings and is hydrolyzed producing water-soluble PVA (7.46). The PVA may be reacted with butyraldehyde to produce poly(vinyl butyral) used as the inner lining of safety glass.



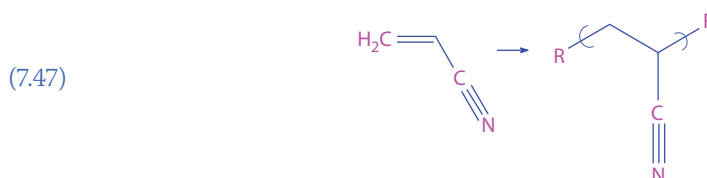
PVA itself has many uses and serves as a major ingredient in many of the Elmer's glues (Picture 7.1).

When a monomer such as acrylonitrile is polymerized in a poor solvent, macroradicals precipitate as they are formed (7.47). Since these are “living polymers,” the polymerization continues as more acrylonitrile diffuses into the precipitated particles. This heterogeneous solution polymerization has been called “precipitation polymerization.” Polyacrylonitrile (PAN) (produced under the trade name Acrilan) cannot be colored, so small amounts of a comonomer such as styrene,



PICTURE 7.1 Many glue adhesives are poly(vinyl alcohol)-based synthetic glues.

vinyl chloride, or vinylidene chloride, are added to allow the fabrics and textiles to be colored. These copolymers are called “modacrylics.” The use of vinylidene chloride and vinyl chloride gives a product, such as a carpet or wig, increased flame resistance.



7.4.4 EMULSION POLYMERIZATION

Many water-soluble vinyl monomers may be polymerized by the emulsion polymerization technique. This technique, which differs from suspension polymerization in the size of the suspended particles and in the mechanism, is widely used for the production of a number of commercial plastics and elastomers. While the particles in the suspension range from 10 to 1000 nm, those in the emulsion process range from 0.05 to 5 nm in diameter. The small beads produced in the suspension process may be separated by filtering, but the latex produced in emulsion polymerization is a stable system in which the charged particles cannot be recovered by ordinary separation procedures.

Since relatively stable macroradicals are produced in the emulsion process, the termination rate decreases and a high-molecular-weight product is rapidly produced. It is customary to use a water-soluble initiator such as potassium persulfate, an anionic surfactant such as sodium stearate, and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40°C–70°C. When the concentration of soap exceeds the critical micelle concentration, the molecules are present as micelles in which the hydrophilic carboxylic acid ends are oriented toward the water–micelle interface and the lyophilic hydrocarbon ends are oriented toward the center of the micelle. The micelles are present as spheres with a diameter of 5–10 nm when the soap concentration is less than 2%. However, with the higher concentrations typically employed, the micelles resemble aggregates of rods that are 100–300 nm in length.

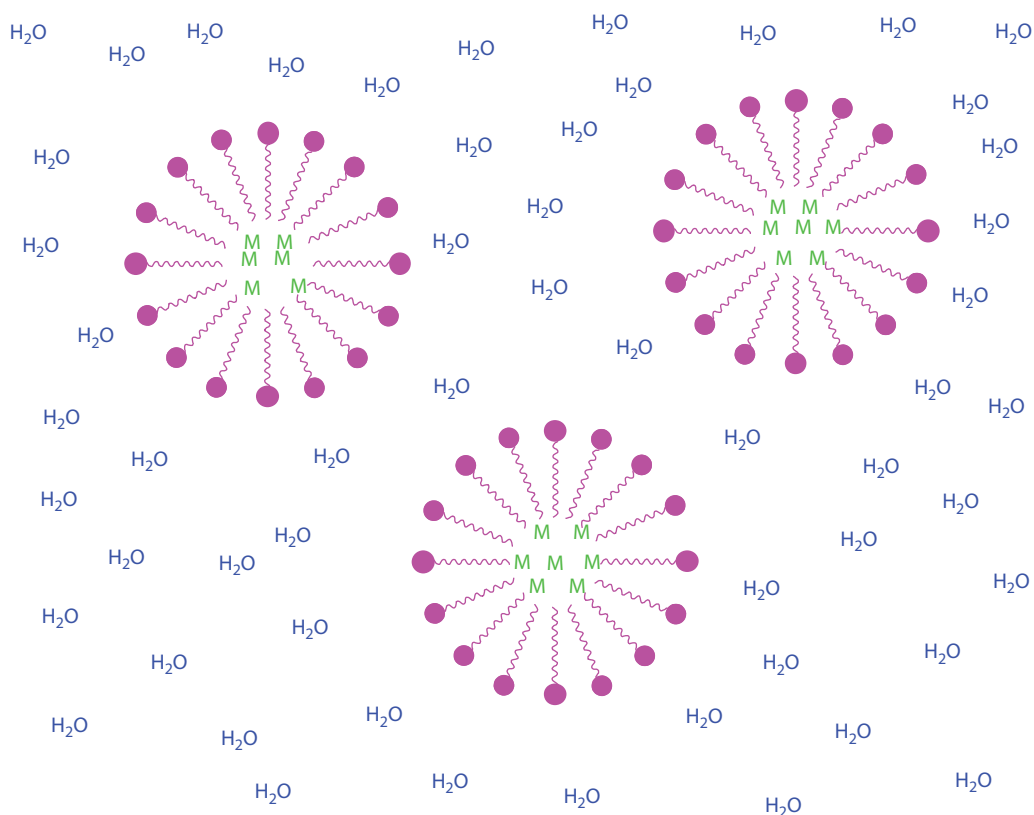


FIGURE 7.3 Micelles swollen with solubilized monomer. As the concentration increases, the micelles change from spherical, as shown, to more rodlike in appearance.

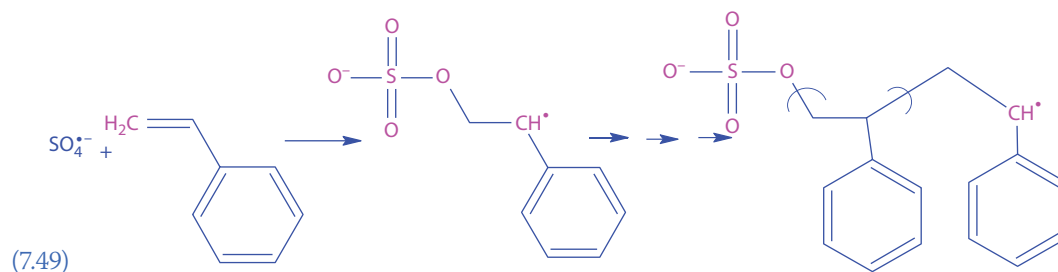
As shown in Figure 7.3, the water-insoluble monomer, M, is attracted to the lyophilic ends in the micelles, causing the micelles to swell. The number of swollen micelles per milliliter of water is on the order of 10^{18} . However, at the initial stages of polymerization (phase I) most of the monomer is present as globules that resemble those observed in suspension polymerization.

Since the initiation of polymerization takes place in the aqueous phase, essentially no polymerization occurs in the globules. Thus, they serve primarily as a reservoir of monomer supplied to the micelles to replace monomer converted to polymer. The number of droplets per milliliter of water is on the order of 10^{11} . Hence, since there are 10 million times as many micelles as droplets, the chance of initiation of monomer in a droplet is very small and the chance that more than one growing chain occurs within the same droplet is very, very small.

The persulfate ion undergoes homolytic cleavage producing two sulfate ion radicals;



The sulfate ion radical then initiates polymerization, here with a styrene monomer eventually forming a PS oligomer radical and eventually a PS radical (7.49):



According to a theory proposed by Harkins and refined by Smith and Ewart, the first stages of propagation in an emulsion system also take place in the aqueous phase to produce a more lyophilic surface oligoradical. When the DP of the PS oligoradical is 3–5, its solubility is much like that of styrene, and it migrates to the swollen micelle where propagation continues with the styrene molecules already present. According to the accepted theories, each micelle can accommodate only one free radical, as noted before, and until a second one enters and terminates the propagation reaction through coupling, propagation continues to take place in the micelles. From a statistical point of view, only one-half of the micelles ($N/2$) will contain growing chains at any one time. It should also be noted that since propagation occurs in the micelles, the rate of polymerization will be proportional to the number of micelles present, that is, the rate is proportional to the soap concentration.

As the micelles grow by absorption of more monomer and formation of polymer, they become relatively large particles that absorb soap from micelles that have not been inoculated or stung by oligoradicals. Thus, in stage II, when about 20% of the monomer has been converted to polymer, the micelles disappear and are replaced by large, but fewer, monomer–polymer particles.

Polymerization continues in stage II, and monomer continues to be supplied to the particles by the droplets in the aqueous phase. These droplets disappear when about 30% of the monomer has been converted to polymer. Polymerization continues in stage III after about 60% conversion, but all monomer must now be supplied to the macroradicals by a diffusion process in the micelles.

The rate of sulfate decomposition is described as

$$(7.50) \quad R_d = k_d [S_2O_8^{-2}]$$

The rate of initiation is then

$$(7.51) \quad R_i = k_i [SO_4^{\bullet-}][M] = 2k_d f [S_2O_8^{-2}]$$

The rate of propagation in the micelles is similar to that described for other free radical chain growth, but since the free radical concentration is equal to the number of active micelles, the value of $N/2$ is used instead of $[M^*]$. Thus, the rate of propagation is dependent on the number of micelles present.

$$(7.52) \quad R_p = k_p [M][M^*] = k_p [M] (N/2)$$

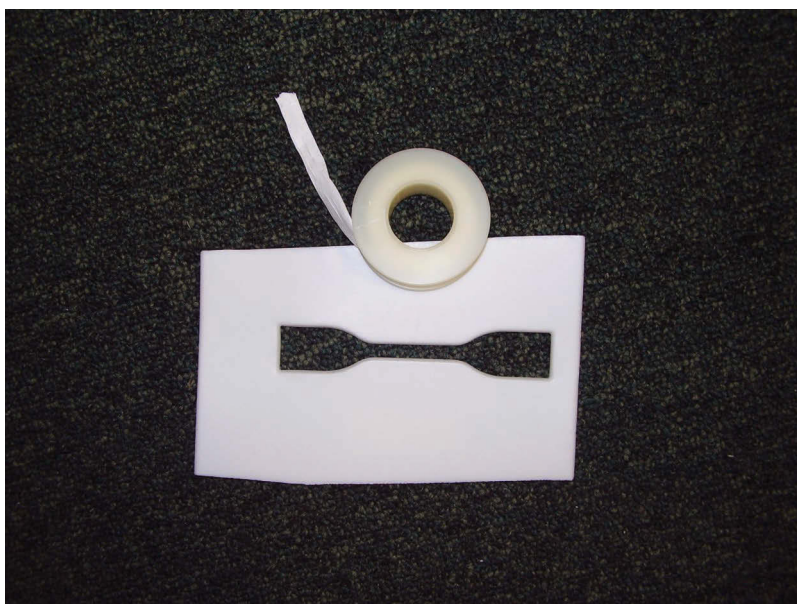
The rate of production of free radicals at 50°C is about 10^{13} radicals/mL per 1 second. Thus, since there are 10^5 micelles for every free radical produced in 1 second, inoculation of any of the 10^{18} micelles/mL is infrequent. Hence, since propagation is a very fast reaction, long chains are produced before termination by coupling, which takes place as the result of the entrance of a new oligoradical in the active micelle. The DP is also proportional to the number of active micelles ($N/2$):

$$(7.53) \quad \overline{DP} = \frac{R_p}{R_i} = \frac{k_p (N/2)}{k_i [SO_4^{\bullet-}]}$$

7.5 FLUORINE-CONTAINING POLYMERS

7.5.1 POLYTETRAFLUOROETHYLENE

Polytetrafluoroethylene, better known by its trade name Teflon (Picture 7.2), was accidentally discovered by Roy J. Plunkett, a DuPont chemist who had just received his PhD from Ohio State 2 years before. He was part of a group searching for nontoxic refrigerant gases. On April 6, 1938, he and his assistant, Jack Rebok, had filled a tank with tetrafluoroethylene. After some time, they opened the valve but no gas came out. The tank weight indicated that there was no weight



PICTURE 7.2 Polytetrafluoroethylene from which a dogbone used for property testing has been cut and polytetrafluoroethylene tape.

loss—so what happened to the tetrafluoroethylene. Using a hacksaw, they cut the cylinder in half and found a waxy white powder. He correctly surmised that the tetrafluoroethylene had polymerized. The waxy white powder had some interesting properties. It was quite inert toward strong acids, bases, and heat and was not soluble in any attempted liquid. It appeared to be quite “slippery.”

Little was done with this new material until the military, working on the atomic bomb, needed a special material for gaskets that would resist the corrosive gas uranium hexafluoride that was one of the materials being used to make the atomic bomb. General Leslie Groves, responsible for the U.S. Army’s part in the atomic bomb project, had learned of DuPont’s new inert polymer and had DuPont manufacture it for them.

Teflon was introduced to the public in 1960 when the first Teflon-coated muffin pans and frying pans were sold (Picture 7.3). Like many new materials, problems were encountered. Bonding to the surfaces was uncertain at best. Eventually, the bonding problem was solved. Teflon is now used for many other applications including acting as a biomedical material in artificial corneas; substitute bones for nose, skull, hip, nose, and knees; and ear parts, heart valves, tendons, sutures, dentures, and artificial tracheas. It has also been used in the nose cones and heat shield for space vehicles and for their fuel tanks.

Over one-half million vascular graft replacements are performed yearly. Most of these grafts are made of PET and Polytetrafluoroethylene (PTFE). These relatively large diameter grafts work when blood flow is rapid, but they generally fail for smaller vessels.

Polytetrafluoroethylene is produced by the free radical polymerization process. While it has outstanding thermal and corrosive resistance, it is a marginal engineering material because it is not easily machinable. It has low tensile strength, resistance to wear, and it has low creep resistance. Molding powders are processed by press and sinter methods used in powder metallurgy. It can also be extruded using ram extruder techniques.

PTFE is a crystalline polymer with melting typically occurring above 327°C . Because it is highly crystalline, it does not generally exhibit a noticeable T_g .

The C–F bond is one of the strongest single bonds known with a bond energy of 485 kJ/mol. While it is structurally similar to linear polyethylene (PE), it has marked differences. Because of the small size of hydrogen, PE exists as a crankshaft backbone structure. Fluorine is a little larger (atomic radius of F = 71 picometers and for H = 37 picometers) than hydrogen causing the Teflon backbone to be helical forming a complete twist every 13 carbon atoms. The size of the fluorine is



PICTURE 7.3 Polytetrafluoroethylene-coated cookware.

sufficient to form a smooth “protective” sheath around the carbon backbone. The concentration of F end groups is low in ultrahigh-molecular-weight PTFE contributing to its tendency to form crystals.

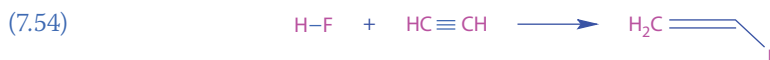
The electron density of PE and PTFE are also different. The electronegativity value for C is 2.5, F = 4.0, and for H = 2.1. Thus, the electron density on the fluorine surface of PTFE is greater than that for PE.

For high-molecular-weight linear PE, the repeat unit length is about 0.254 nm forming crystalline portions with a characteristic thickness of about 10 nm. The chain length for tough solids from PE is about 4.5 times the crystalline thickness. Thus, tough solids occur at molecular weights greater than 5000 g/mol or chain lengths greater than about 45 nm. In comparison, the repeat unit length for PTFE is about 0.259 nm. The crystalline thicknesses for PTFE are about 100–200 nm or much thicker than for PE. Chain lengths for tough solids are about 4.5 times the crystalline thickness. Thus, much greater chain sizes, about 200,000–400,000 Da, are required to produce tough solids. The greater size of the crystalline portions also probably contributes to its higher T_m and greater difficulty in processing. The crystal thickness of PTFE is about 10–20 times the crystal thickness found for most other semicrystalline polymers such as PE.

At low molecular weights, PTFE is waxy and brittle. To achieve good mechanical properties ultrahigh molecular weights on the order of 10 million Da are usually needed. These long chains disrupt crystal formation because they are longer than a single crystal. But the long chain lengths connect the crystals together adding to their strength. But these long chains result in extremely high viscosities so that ultrahigh-molecular-weight PTFE does not flow when melted and is, thus, not melt processable. Form restrictive and costly methods are used to produce products from PTFE.

7.5.2 POLY(VINYL FLUORIDE)

While vinyl fluoride was prepared about 1900, it was believed resistant to typical “vinyl” polymerization. German scientists prepared vinyl fluoride through reaction of acetylene with hydrogen fluoride in the presence of catalysts in 1933:



It was not until 1958 that DuPont scientists announced the polymerization of vinyl fluoride forming poly(vinyl fluoride) (PVF) (Equation 7.55). Polymerization is accomplished using peroxide catalysts in water solutions under high pressure:



In comparison to PTFE, PVF is easily processable using a variety of techniques used for most thermoplastic materials. It offers good flame retardancy, presumably due to the formation of HF that assists in the control of the fire. Thermally induced formation of HF is also a negative factor because of its toxicity. As in the case of PVC, elimination of the hydrogen halide promotes formation of aromatic polycyclic products that themselves are toxic.

The difference in electronegativity between the adjacent carbons because of the different electronegativities of H and F results in the C–F bond being particularly polar resulting in it being susceptible to attack by strong acids. The alternating bond polarities on the PVF chain give it a tight structure resulting in PVF films having a low permeability. This tight structure also results in good solvent resistance, resistance to cracking, and resistance to fading.

Friction and wear are important-related characteristics. If a material has a high friction, then it will generally have a shorter wear time because water or other friction event chemicals pass over the material with the higher friction causing greater wear. The friction eventually “wears” away polymer chains layer by layer. The engineering laws of sliding friction are simple. According to Amontons’ laws, the friction F between a body (rain drop, wind, or board rubbing against the material) and a plane surface (the polymeric material) is proportional to the load L and independent of the area of contact A . The friction of moving bodies is generally less than that of a static body. The kinetic friction is considered independent of the velocity. The coefficient of friction is defined as F/L . Polymers show a wide range of coefficients of friction so that rubbers exhibit relatively high values ($BR = 0.4$ – 1.5 and $SBR = 0.5$ – 3.0), whereas some polymers such as PTFE (0.04 – 0.15) and PVF (0.10 – 0.30) have low values.

The low coefficient of friction for PVF results in materials coated with it remaining somewhat free of dirt and other typical contaminants allowing PVF-coated materials to be less frequently cleaned. It is essentially self-cleaning as rain carries away dust and other particulates including bird droppings, acid rain, and graffiti. The low friction also results in longer lifetimes for materials coated with the PVF and for the PVF coating itself.

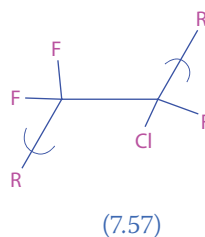
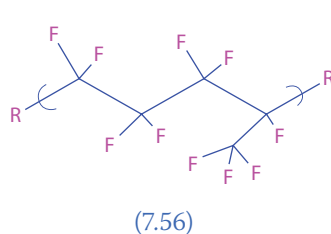
PVF has a T_g of about -20°C remaining flexible over a wide temperature range (from about -20°C to 150°C), even under cold temperatures. Because of its low coefficient of friction and tightly bound structure, it retains good strength as it weathers. Films, in Florida, retain much of their thickness even after about a decade losing less than 20% of their thickness. To increase their useful lifetimes, relatively thick films, such as 1 mil, are generally employed. The “slickness” also acts to give the material a “natural” mildew resistance.

Unlike PVC that requires plasticizers to be flexible, PVF contains no plasticizers and does not “dry out” like PVC. PVF, because of its higher cost in comparison to PE and PP, is used as a coating and selected “high-end” bulk applications such as films. Films are sold by DuPont under the trade name Tedlar. Teldar is used in awnings, outdoor signs, roofing, highway sound barriers, commercial building panels, and solar collectors. It is used as a fabric coating, protecting the fabric from the elements. PVF is resistant to UV-related degradation and unlike PVC, it is inherently flexible. While transparent, pigments can be added to give films and coatings with varying colors. Protective coatings are used on plywood, automotive parts, metal siding, lawn mower housings, house shutters, gutters, electrical insulation, and in packaging of corrosive chemicals. PVF has piezoelectric properties generating a current when compressed.

7.5.3 OTHER FLUORINE-CONTAINING POLYMERS

The processability of fluorine-containing polymers is improved by replacement of one or more of the F atoms. Replacing one of eight fluorine atoms with a trifluoromethyl group gives a product

called FEP or Viton, actually a copolymer of tetrafluoroethylene and hexafluoropropylene (7.56). Polytrifluoromonoethylenes (CTFE, Kel F; 7.57), in which one fluorine atom has been replaced by a chlorine atom, has a less regular structure and is thus more easily processed. Poly(vinylidene fluoride) (Kynar) is also more easily processable but less resistant to solvents and corrosives.



Ethylene tetrafluoroethylene (ETFE) (7.58) was developed by DuPont in the 1970s to be an aeronautical insulation. ETFE was made from a waste product of lead and tin mining. ETFE is being used in a variety of applications. It is used as a covering for electrical wiring, inflated in pillows as a building material, and as glass-like sheets that have an equal to and better light transmission compared with glass. In the nuclear industry, it is used for tie and cable wraps. Recently, it has become a material in innovative building exteriors including use in the Eden Project, Cornwall; Kansas City Power and Light District, Kansas City; whale-shaped aquarium on New York's Coney Island; and most prominently displayed in Beijing's National Stadium also called the Bird's Nest. The Bird's Nest appears to be composed of loosely woven twigs. "Pillows" made from ETFE fill the spaces between and above the "twigs." It is also used to make the pneumatic panels that cover the outside of the soccer stadium Allianz Arena in Munich and the Beijing National Aquatics Center, also called the Water Cube, for the 2008 Olympics. ETFE panels are also employed as a dual laminate bonded with fiber-reinforced polymer composites that are used as corrosive protective liners in pipes, vessels, and tanks.



ETFE has high corrosion resistance and good strength over a wide range of temperatures of approximately -150°C to 150°C . Compared to glass, ETFE film is 1% of its weight, transmits more light, and is less expensive to install. It is highly resilient able to bear 400 times its own weight. It is recyclable and self-cleaning because of the slickness brought about due to the presence of the tetrafluoroethylene units. On the negative side, as with most fluorine-containing polymers, combustion results in the release of highly corrosive HF.

7.6 POLYSTYRENE

Styrene monomer was discovered by Newman in 1786. The initial formation of PS was made by Simon in 1839. While PS was formed almost 175 years ago, the mechanism of formation, described in Sections 7.1 through 7.3, was not discovered until the early twentieth century. Staudinger, using styrene as the principal model, identified the general free radical polymerization process in 1920. Initially, commercialization of PS, as in many cases, awaited the ready availability of the monomer. While ethyl benzene was available, it underwent thermal cracking rather than dehydrogenation until the appropriate conditions and catalysts were discovered. Dow first successfully commercialized PS formation in 1938. While most commercial PS has only a low degree of stereoregularity, it is rigid and brittle because of the resistance of the more bulky phenyl-containing units to move in comparison, for example, to the methyl-containing units of polypropylene. This is reflected in a relatively high T_g of about 100°C for PS. It is transparent because of the low degree of crystalline formation.

While PS is largely commercially produced using free radical polymerization, it can be produced by all four of the major techniques—*anionic*, *cationic*, *free radical*, and *coordination-type* systems. All of the tactic forms can be formed employing these systems. The most important of the tactic forms is *syndiotactic PS*, *sPS*. *Metallocene-produced sPS* is a *semicrystalline* material with a T_m of 270°C . It was initially produced by Dow in 1997 under the trade name *Questa*. It has good chemical and solvent resistance in contrast to “regular” PS that has generally poor chemical and solvent resistance because of the presence of voids that are exploited by the solvents and chemicals.

Physical properties of PS are dependent on the molecular weight and presence of additives. While higher-molecular-weight PS offers better strength and toughness, it also offers poorer processability. Low-molecular-weight PS allows good processability but poorer strength and toughness. Generally, a balance is sought where intermediate chain lengths are used. Typically, employed chain lengths are on the order of 1500–3500 with standard molecular weight distributions of about 2.2–3.5. Small amounts of plasticizers are often used to improve processability.

PS is used in the manufactures of many of our everyday plastics such as the CD and DVD cases that are also used for many other applications (Picture 7.4). Styrene is employed in the formation of a number of co- and terpolymers. The best known is the terpolymer *ABS*.

PS is produced in three forms—*extruded PS (XPS)*, *expanded PS (EPS) foam*, and *XPS foam*. EPS was developed by the Koppers Company in Pittsburgh, Pennsylvania, in 1959. XPS foam insulation was developed by Dow Chemical and sold under the trade name *Styrofoam*. This term is often used for many other EPS materials. EPS and XPS are similar and both generally contain a mixture of 90%–95% PS and 5%–10% gas (also referred to as a blowing agent), generally pentane, nitrogen, or carbon dioxide. The solid plastic is heated typically using steam followed by introduction of the gas. EPS is produced from PS beads containing the entrapped blowing agents. When heated, the blowing agent turns to a gas expanding resulting in the individual beads expanding and fusing together. XPS foam is similarly formed except the blowing agents become gaseous as the mixture emerges from an extruder giving a more continuous product in comparison to EPS.

As noted, XPS foam is often known by its trade name *Styrofoam*. XPS has air inclusions giving the material some flexibility, low thermal conductivity, and a low density. It is widely used as commercial and residential insulation. In construction, it is also used to make ornamental pillars that are subsequently coated with a harder material. Under roads and buildings it is employed to prevent soil disturbance due to weathering. Life rafts are generally made from XPS but can be made from EPS.



PICTURE 7.4 CD cases made from injection-molded polystyrene.



PICTURE 7.5 Polystyrene packing material in most colors but usually white.

Styrofoam structural insulation sheathing (SIS) has recently been introduced by Dow. SIS is a wall system that combines structural and water resistance with insulation properties. It is made with about 80% recycled material and believed to reduce energy consumption by about 10%.

EPS foam is incorrectly best known to the general public as Styrofoam cups, coolers, and egg containers. EPS can be generally distinguished from Styrofoam by the presence of small beads or spheres that are present in the EPS and missing in the XPS. It is also used to make a number of other products such as inexpensive surfboards and other water and pool floating devices. It is used to make packing peanuts (Picture 7.5) and molded packing material for cushioning items such as TVs, computers, and stereo equipment.

XPS is used for objects where a somewhat rigid inexpensive plastic material is needed such as plastic Petri dishes, plastic test tubes, plastic model kits, CD jewel cases, toys, housewares, and appliance parts. Medical products are sterilized after the product is made using irradiation or treatment with ethylene oxide.

Legislation was put in place in some states to insure the recycling of PS. Interestingly, some of this legislation was written such that all PS had to be recycled within some period of time such as a year. This legislation was changed to reflect the real concern of fast food containers when it was pointed out that less than 10% PS is used in this manner and that well over twice as much was used as house insulation that should not be recycled every year or so.

7.7 POLY(VINYL CHLORIDE)

PVC is one of the three most abundantly produced synthetic polymers. It is one of the earliest commercial polymers. In 1835, Justus von Liebig and his research student Victor Regnault reacted ethylene dichloride with alcoholic potash forming the monomer vinyl chloride. Later, Regnault believed he polymerized vinyl chloride but latter studies showed it to be poly(vinylidene chloride). In 1872, E. Baumann exposed vinyl chloride sealed in a tube to sunlight and produced a solid, PVC. Klasse, in Germany, found that vinyl chloride could be made by addition of hydrogen chloride to acetylene in a system that could be scaled up for commercial production. (Today most vinyl chloride is made from the oxychlorination reaction with ethylene.) By WWI, Germany was producing a number of flexible and rigid PVC products. During WWI, Germany used PVC as a replacement for corrosion-prone metals.

Waldo Semon was responsible for bringing many of the PVC products to market. As a young scientist at BF Goodrich, he worked on ways to synthesize rubber and to bind the rubber to metal.

In his spare time, he discovered that PVC, when mixed with certain liquids, gave an elastic-like, pliable material that was rain proof and fire resistant and that did not conduct electricity. Under the trade name Koroseal, the rubbery material came into the marketplace, beginning about 1926, as shower curtains, raincoats, and umbrellas. During WW II, it became the material of choice to protect electrical wires for the Air Force and Navy. Another of his inventions was the synthetic rubber patented under the name Ameripol that was dubbed “liberty rubber” since it replaced natural rubber in the production of tires, gas masks, and other military equipment. Ameripol was a butadiene-type material.

As a side note, there is today a debate concerning the use of chlorine-containing materials and their effect on the atmosphere. This is a real concern and one that is being addressed by industry. PVC and other chloride-containing materials have in the past been simply disposed of through combustion that often created unwanted hydrogen chloride. This practice has largely been stopped but care should be continued to see that such materials are disposed of properly. Further, simply outlawing of all chloride-containing materials is not possible or practical. For instance, we need common table salt for life and the common table salt is sodium chloride. Chlorine is widely used as a water disinfectant both commercially (for our drinking water) and for pools. Further, PVC is an important material that is not easily replaced. Finally, the amount of chloride-containing residue that is introduced into the atmosphere naturally is large in comparison to that introduced by PVC. Even so, we must exercise care as we want to leave a better world for our children and grandchildren, so a knowledge-based approach must be taken.

Another health concern is the presence of certain plasticizers. As noted in the following discussion, PVC employs a large amount of additives including a variety of plasticizers. We do not live in a risk-free society but some risks should be eliminated or minimized. One group of plasticizers of interest is the phthalate plasticizers. As with other health concerns, infant care is of greatest concern. Vinyl IV bags are often used in neonatal intensive care units. FDA has requested that manufacturers eliminate the use of questionable plasticizers for the production of these bags. Another answer is simply eliminating vinyl IV bags using another material for construction of these bags. Further, baby and children toys should be constructed from materials that do not contain these plasticizers. Another group that is at particular risk is the critically ill or injured patients. Again, special care should be exercised when dealing with special groups of people. As we are dealing with toxic materials, we need to remember that all materials can be harmful if present in the wrong concentrations and/or locations. Even so, where we can we might minimize exposure to known potentially toxic materials.

Because of its versatility, some unique performance characteristics, ready availability, and low cost, PVC currently is the third largest produced synthetic polymer behind PE and polypropylene. PVC materials are often defined to contain 50% or more by weight vinyl chloride units. PVC is generally a mixture of a number of additives and often other units such as ethylene, propylene, vinylidene chloride, and vinyl acetate. Structurally similar products, but with differing properties, are made from the chlorination of PE but almost all PVC is made from the polymerization of vinyl chloride. Typical homopolymers are about 400–1000 units long.

PVC is commercially produced by a number of techniques but mainly suspension, emulsion, bulk, and solution polymerization. Typically, product properties and form can be tailored through the use of a particular synthetic process and conditions. Particulate architecture is then controlled to achieve materials with specific sizes and distributions for specific uses and applications. Because of the tendency of PVC to split off hydrogen chloride, forming materials with high char at relatively low general processing temperatures, special care is taken with respect to temperature control and particulate architecture that allows ready processing of PVC by most of the common processing techniques.

Tacticity of the PVC varies according to the particular reaction conditions but generally manufactures favor a syndiotactic form with many PVC materials being about 50% sPVC. The reported amount of crystallinity is in the range of 5%–10%. This allows for a material with some strength but one with sufficient amorphous regions to retain good flexibility.

PVC, in comparison to many other polymers, employs an especially wide variety of additives. For instance, a sample recipe or formulation for common stiff PVC pipe such as used in housing and irrigation applications may contain in addition to the PVC resin, tin stabilizer, acrylic



PICTURE 7.6 Poly(vinyl chloride) piping and fittings.

processing aid, acrylic lubricant-processing aid, acrylic impact modifier, calcium carbonate, titanium dioxide, calcium stearate, and paraffin wax (Picture 7.6). Such formulations vary according to the intended processing and end use. In such nonflexible PVC materials, the weight amount of additive is on the order of 5%–10%.

As noted before, there is a tendency for PVC to undergo elimination of hydrogen chloride when heated. The most labile chlorine atoms are those at tertiary or terminal sites. Once the initial chloride is eliminated, continued unzipping occurs with the formation of unsaturated backbone sites and the evolution of hydrogen chloride. The purpose of the stabilizer is to cap unzipping sites by substitution of more stable groups for the evolved chloride as depicted here (7.59).



Some of the tin stabilizers are based on oligomeric materials first made by Carraher and coworkers. These oligomeric materials are essentially “nonmigratable.”

A sample formula for a flexible upholstery fabric covering might contain PVC resin, medium molecular weight polymeric plasticizer, stearic acid lubricant, calcium carbonate, pigment, anti-mony oxide, linear phthalate ester, epoxidized soy bean oil, and linear phthalate ester. Here the weight amount of additive is in the range of 40%–70% by weight with the plasticizer often being on the order of about 60%.

PVC has a built in advantage over many other polymers in which it is itself flame resistant. About 50% of PVC is used as rigid pipe. About 70% of the water pipes in the United States are PVC. About 75% of the sewer pipes are PVC. Other uses of rigid PVC are as pipe fittings, electrical outlet boxes, and automotive parts. Uses of flexible PVC include in gasoline-resistant hose, hospital sheeting, shoe soles, electrical tape, stretch film, pool liners, vinyl-coated fabrics, roof coatings, refrigerator gaskets, floor sheeting, and electrical insulation and jacketing. A wide number of vinyl chloride copolymers are commercially used. Many vinyl floor tiles are copolymers of PVC.

Many flat sheet signs are made of PVC. Films are also formed from PVC. Many of these signs and films are simply referred to as vinyl. These films and sheets form many of our commercial signs and markings on vehicles. Unplasticized or rigid PVC is used in the construction industry as a siding simply known as “**vinyl siding**.” It is also used to repair window frames and sills and fascia. It is also widely used in the construction of plastic gutters, downpipes, and drainpipes.

The flame resistance of PVC is a mixed blessing. In a fire, the PVC emits hydrogen chloride with the chlorine scavenging free radicals helping eliminate the fire. Hydrogen chloride fumes present a health concern when we breathe them. In a fire moisture helps dilute the hydrogen chloride causing it to settle on the cooler surfaces rather than remaining air borne. Even so, in closed structures such as tunnels alternative materials are advised.

7.8 POLY(METHYL METHACRYLATE)

PMMA (7.43) is also referred to as acrylic glass or fiber. It was initially developed in 1928 and became commercially available in 1933 by Rohm and Hass. It is a thermoplastic transparent plastic or fiber produced by the polymerization of methyl methacrylate using emulsion, solution, and bulk free radical polymerization. *Acrylic fiber* refers to both fibers made from PMMA and also those made from PAN (Picture 7.7). PMMA is often used as an alternative to glass and sold under a number of trade names including Lucite, Plexiglas, Acrylex, Acrylite, Oroglass, and Vitroflex. When completely burned, the products are carbon dioxide and water making it an environmentally positive material in this regard.

In comparison to glass, PMMA is lighter and has greater impact strength than glass or PS but less than that of polycarbonate. It is more easily scratched than glass but has optical properties similar to glass in that it transmits up to 98% of light with a low reflection. It is inferior to glass with respect to environmental stability and resistance to solvent, though its environmental stability is better than that of most other plastics.

As already noted, PMMA is often used as an alternative to glass. PMMA is used in the exterior lenses of automobiles and trucks (Picture 7.8). The spectator protection shield in ice hockey stadiums is made of PMMA. The windows of many aircraft and windows of police vehicles for riot control are PMMA as are many motorcycle helmet visors.

PMMA is also used in medicine. PMMA has a good compatibility with human tissue and has been used for replacement of intraocular lenses in eyes. Hard contact lenses are often composed of PMMA. Bone cement containing PMMA is used to connect bond implants and remodel lost bone. PMMA has a Young's modulus near that of bone, so it does a good job of load sharing with the native bone. Dentures are often PMMA. In cosmetic surgery, colored PMMA microspheres are implanted to reduce wrinkles and scars.



PICTURE 7.7 Acrylic sweaters from Poly(methyl methacrylate).



PICTURE 7.8 Poly(methyl methacrylate) tail light coverings.

Artistic uses of PMMA are many. Acrylic paints are largely PMMA suspended in water. Because PMMA is hydrophobic, materials are added to allow the suspension to occur (Picture 7.9). Salvador Dali has used PMMA plastic sheets to paint on.

PMMA has many other uses including as artificial fingernails, bodies of electric guitars and basses, light guide in electrical devices, short distance optical fibers, drums called Vistalites that were used by the Led Zeppelin drummer John Bonham, and extensively either the backside, backplate, letters or design, or faceplate in the sign business. The high heels of shoes are often made of PMMA.

PMMA is also used in the semiconductor industry as a resist in the electron beam lithography process. For instance, a semiconductive wafer is coated with a PMMA-containing solution.



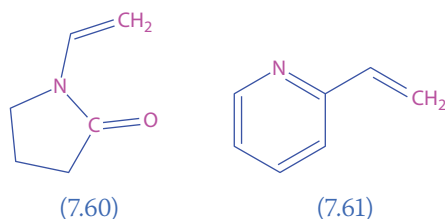
PICTURE 7.9 Mixed media—pen and ink and water color (acrylic water colors). Iris by the author. Acrylic water colors.

Patterns are then cut onto this surface using an electron beam, deep UV light, or x-rays. The areas exposed to this radiation contain degraded PMMA that is removed by a chemical developer making it a positive photoresist. PMMA allows precision etching with nanoscale patterns created.

7.9 POLYACRYLONITRILE

PAN (7.47) forms the basis for a number of fibers and copolymers. As fibers, they are referred to as acrylics or acrylic fibers. The development of acrylic fibers began in the early 1930s in Germany, but they were first commercially produced in the United States by DuPont (Orlon) and Monsanto (Acrilan) about 1950.

Because of the repulsion of the cyanide groups, the polymer backbone assumes a rodlike conformation. The fibers derive their basic properties from this stiff structure of PAN where the nitrile groups are randomly distributed about the backbone rod. Because of strong bonding between the chains, they tend to form bundles. Most acrylic fibers actually contain small amounts of other monomers such as methyl acrylate and methyl methacrylate. Because they are difficult to dye, small amounts of ionic monomers, such as sodium styrene sulfonate, are often added to improve their dyeability. Other monomers are also employed to improve dyeability. These include small amounts (about 4%) of more hydrophilic monomers such as *N*-vinyl-2-pyrrolidone (7.60), methacrylic acid, or 2-vinylpyridine (7.61).



Acrylic fibers are used as an alternative to wool for sweaters (Picture 7.10). PAN is also used in the production of blouses, blankets, rugs, curtains, shirts, craft yarns, and pile fabrics used to simulate fur.



PICTURE 7.10 Acrylic sweaters.

Because of the presence of the cyano group, there can be concern that when burned, HCN can be given off. Contrary to this, at temperatures above 160°C, PAN begins forming cyclic imines that dehydrogenate forming dark-colored heat-resistant fused ring polymers with conjugated C=C and C=N bonding. This is described in Section 10.12. Thus, rather than forming toxic HCN, PAN forms thermally stable intermediates that act to curtail burning.

Fibers with more than 85% acrylonitrile units are called acrylic fibers, but those containing 35%–85% acrylonitrile units are referred to as modacrylic fibers. The remainder of the modacrylic fibers are derived from comonomers such as vinyl chloride or vinylidene chloride that are specifically added to improve flame resistance.

7.10 SOLID-STATE IRRADIATION POLYMERIZATION

There are numerous examples of solid-state polymerizations. Here we will briefly describe examples based on addition polymers. Generally, the crystalline monomer is irradiated with electrons or some form of high energy radiation such as gamma or x-rays. Since many monomers are solids only below room temperature, it is customary to begin irradiation at lower temperatures with the temperature only raised after the initial polymerization occurs. (Some reactions are carried to completion at the lower temperature.) After polymerization, monomer is removed. Table 7.7 contains a list of some of the common monomers that undergo solid-state irradiation polymerization.

This approach can offer several advantages. First, polymers can be formed from monomers that do not give polymer under more typical reaction conditions. Second, under some cases, the crystalline structure acts as a template giving order that might be difficult to otherwise achieve. Third, removal and interference by solvent or additives is eliminated since they are not present. Fourth, the polymers produced by this technique are often different from those from the same monomer except produced using typical reaction techniques.

7.11 PLASMA POLYMERIZATIONS

Organic and inorganic molecules can be placed in the vapor state either through heating, low pressure, simply spraying, or some combination of these. These molecules are then subjected to some ionizing energy that forms active species that react with one another eventually depositing themselves on a surface. Often the products are polymeric with complex structures. The term plasma polymerization is generally used to describe the process resulting in surface film formation, while the term deposition is generally used to describe the deposition of powdery particles formed in the gas phase. Others describe plasma polymerization as that polymerization that occurs at high rates in the gas phase resulting in powder formation and deposition as any sorption occurring on the surface. In truth, it is difficult to separate the two reaction sequences because active molecules can react both in the gaseous phase upon collision and on the surface.

TABLE 7.7 Monomers That Undergo Solid-State Irradiation Polymerization

Styrene	Formaldehyde
Acetaldehyde	Acrylic acid (and salts)
Methacrylic acid (and salts)	Trioxane
1,3-Butadiene	3,3-Bis(chloromethyl)cyclohexane
Isoprene	Acrylonitrile
Acrylamide	Beta-propiolactone
Diacetylenes	

Plasma environments are often created using plasma jets, ion beams, glow discharges, corona discharges, laser-induced plasmas, and electron beams. Low-temperature plasmas can also be created using radio frequency, audio frequency, microwave, or direct current energy sources. In general terms, the molecules enter the reactor as neutral species. They become reactive species as electronic energy is transferred to them. The reactive species can be ions, free radicals, or excited molecules. Reaction can occur in the gaseous phase and/or at the solid surface. Commercially, reactors often consist of a low pressure glow discharge of reactive species. Because a small amount of electromagnetic radiation is emitted in the visible region, the term glow discharge was derived.

This approach allows the deposition of thin films at low temperatures. By comparison, polymer deposition generally requires very high temperatures. For instance, the chemical vapor deposition of silicon nitride requires a temperature of about 900°C, whereas the plasma chemical deposition requires a temperature of only 350°C.

A number of typical polymer-forming monomers have been polymerized using plasma polymerization including tetrafluoroethylene, styrene, acrylic acid, methyl methacrylate, isoprene, and ethylene. Polymerization of many nontypical monomers has also occurred including toluene, benzene, and simple hydrocarbons.

Plasma films are usually highly cross-linked, resistant to higher temperatures, and resistance to abrasion and chemical attack, and adhesion to the surface is high. Adhesion to the surface is generally high both because the growing polymer complex can fit the surface contour and thus “lock-itself in” (physical adhesion) and because in many instances, the species are active enough to chemically react with the surface molecules to chemically bond to the surface. The surface can be prepared so that the chemical reaction is enhanced.

Plasma surface treatment of many polymers, including fabrics, plastics, and composites, often occurs. The production of ultrathin films via plasma deposition is important in microelectronics, biomaterials, corrosion protection, permeation control, and adhesion control. Plasma coatings are often on the order of 1–100 nm thick.

SUMMARY

1. For classical free radical polymerizations, the rate of propagation is proportional to the concentration of monomer and the square root of the initiator concentration. Termination usually occurs through a coupling of two live radical chains but can occur through disproportionation. The rate of termination for coupling is directly proportional to initiator concentration. The \overline{DP} is directly proportional to monomer concentration and inversely proportional to the square root of the initiator concentration.
2. The first chains produced are high-molecular-weight products. Within the polymerizing system, the most abundant species are the monomer and polymers chains.
3. Increasing the temperature increases the concentration of free radicals, thus decreasing the chain length. Increasing the temperature increases the rate of polymer formation.
4. The rate-controlling step is the rate of initiation.
5. There is a steady state concentration of growing chains.
6. The kinetic chain length ν is equal to \overline{DP} for disproportionation termination, but $\overline{DP} = 2\nu$ for termination by coupling.
7. Chain transfer reactions almost always decrease \overline{DP} and often will introduce branching as it occurs within or between polymer chains. Solvent also can act as effective chain transfer agents lowering chain length.
8. Vinyl monomers can be polymerized using solution, bulk, suspension, and emulsion techniques. Each has its own characteristic strengths and weaknesses.
9. When polymerizations become viscous, termination slows allowing an increase in the number of growing chains and rate of polymerization. This is known as the gel or Trommsdorff effect. If such reactions are allowed to continue without cooling, explosions are possible.

10. Monomers may be polymerized using a water-soluble initiator while dispersed, by agitation, in a concentrated soap solution. In this emulsion system, initiation occurs in the aqueous phase and propagation occurs in the soap micelles. Since the growing macroradicals are not terminated until a new free radical enters the micelle, high-molecular-weight products are rapidly obtained. The rate of polymerization and \overline{DP} are proportional to the number of activated micelles.
11. Polyfluorocarbons are resistant to heat, solvent, and corrosives. The resistance is greatest in the regularly structured PTFE and decreases as the geometry is upset by substitution of other atoms for fluorine.
12. PVC is an important polymer used for many commercial uses including as pipes for water delivery systems within homes.

GLOSSARY

Backbiting: Hydrogen atom abstraction that occurs when a chain end of a macroradical doubles back on itself forming a more stable hexagonal conformation.

Branch point: Point on a polymer chain where additional chain extension occurs producing a branch.

Bulk polymerization: Polymerization of monomer without added solvents or water; also called neat.

Ceiling temperature (T_c): Characteristic temperature above which polymerization occurs but the polymer decomposes before it is recovered.

Chain stopper: Chain transfer agent that produces inactive free radicals.

Chain transfer: Process in which a free radical abstracts an atom or group of atoms from a solvent, telogen, or polymer.

Chain transfer constant (C_s): Ratio of cessation or termination of transfer to the rate of propagation.

Critical micelle concentration: Minimum concentration of soap in water that will produce micelles.

Dead polymer: Polymer in which chain growth has been terminated.

Disproportionation: Process by which termination occurs as a result of chain transfer between two macroradicals yielding dead polymers.

Half-life time: Time required for half the reactants to be consumed (generally for a first-order reaction).

Heterolytic cleavage: Cleavage of a covalent bond that leaves one electron with each of the two atoms. The products are free radicals.

Homopolymer: Polymer composed of only one repeating unit.

Kel F: Trade name for polytrifluorochloroethylene.

Kinetic chain length: Length of the polymer chain initiated by one free radical.

Macroradicals: Electron-deficient polymers having a free radical present on the chain.

Micelles: Ordered groups of soap molecules in water.

Oligoradical: Low-molecular-weight macroradical.

Piezoelectric: Conversion of mechanical force, such as pressure, into electrical energy.

Plasticizer: High-boiling compatible liquid that lowers T_g and flexibilizes the polymer.

Retarder: Additive that acts as a chain transfer agent producing less active free radicals.

Saran: Trade name for copolymers of vinyl chloride and vinylidene chloride.

SBR: Rubbery copolymer of styrene and butadiene.

Suspension polymerization: Process in which liquid monomers are polymerized in liquid droplets suspended in water.

Telogen: Additive that readily undergoes chain transfer with a macroradical.

Telomer: Low-molecular-weight polymer resulting from chain transfer of a macroradical with a telogen.

Telomerization: Process in which telomers are produced by chain transfer reactions.

Trommsdorff effect: Decrease in termination rate in viscous media that results in higher-molecular-weight polymers being formed.

EXERCISES

1. Use a slanted line to show the cleavage of (a) boron trifluoride–water, (b) sodamide, and AIBN in cationic, anionic, and free radical initiations, respectively.
2. Which type of chain-reaction polymerization is most likely to terminate by coupling?
3. If an initiator has a half-life of 4 h, what percentage of this initiator will remain after 12 h?
4. If some head-to-head configuration is detected in a polymer chain known to propagate by head-to-tail addition, what type of termination has occurred?
5. Which is the better way to increase polymer production rates for free radical reactions in general: (a) increasing the temperature or (b) increasing the initiator concentration?
6. Name three widely used thermoplastics produced by free radical chain polymerization.
7. What effect does the increase of polarity of the solvent have on free radical polymerization?
8. Show the repeat units for (a) PS, (b) PVC, and (c) PMMA.
9. Can you think of any advantage of the Trommsdorff effect?
10. What is the limiting step in free radical chain polymerization?
11. In general, which is more rapid: (a) free radical chain reactions or (b) step reaction polymerizations?
12. If one obtained a yield of 10% polymer after 10 min of polymerizing styrene by a free radical mechanism, what would be the composition of the other 90%?
13. Why is $t_{1/2}$ for all first-order reactions equal to $0.693/k_d$?
14. How could you follow the rate of decomposition of AIBN without directly measuring the rate of polymerization?
15. What is the usual value for the energy of activation of free radical initiation?
16. What is the advantage of producing free radicals by UV radiation?
17. Why is PVC considered negative by some environmentally?
18. If $[M^*]$ is equal to 1×10^{-11} mol/L under steady state conditions, what will $[M^*]$ equal after (a) 30, (b) 60, and (c) 90 min?
19. In general, what is the activation energy in free radical chain propagation of polymer chains?
20. What is the relationship between the rate of propagation and the concentration of initiators $[I]$?
21. When chain transfer with solvent occurs, what effect does this have on the average degree of polymerization?
22. In the free radical polymerization, name two steady state assumptions.
23. What monomer is used to produce PVA?
24. Name one advantage and one disadvantage for the bulk-batch polymerization of PS.
25. Does k_p increase or decrease when the average DP for a single growing chain goes from 10 to 10^4 ?
26. Why is ethylene more readily polymerized by free radical chain polymerization than isobutylene?
27. What is the termination mechanism in free radical polymerization if the average $\overline{DP} = \nu$?
28. The value of ν increases as the polymerization temperature of a specific monomer is increased. What does this tell you about the termination process?
29. In general, what is the activation energy of termination?
30. Why wouldn't you recommend the use of poly- α -methylstyrene for the handle of a cooking utensil?
31. Why is polyfluoroethylene generally known by the public as Teflon?
32. Which would you expect to have the higher-chain-transfer constant: (a) carbon tetrafluoride, or (b) carbon tetrachloride?
33. While the addition of dodecyl mercaptan to styrene causes a reduction in \overline{DP} , the rate of polymerization is essentially unchanged. Explain.
34. Would it be safe to polymerize styrene by bulk polymerization in a 55 gal drum?
35. How do the kinetics of polymerization differ in the bulk and suspension polymerization methods?
36. Since the monomers are carcinogenic, should the polymerization of styrene, acrylonitrile, and vinyl chloride be banned?
37. What are some unusual properties of polyfluoroethylene?

38. Why doesn't polymerization take place in the droplets instead of in the micelles in emulsion polymerization?
39. Why doesn't initiation occur in the micelles in emulsion polymerization?
40. What would happen if one added a small amount of an inhibitor to styrene before bulk polymerization?
41. Name several places you might "run across" PS daily.
42. Why is the T_g of PTFE higher than that of FEP?
43. Why does an increase in soap concentration increase the average DP and R_p in emulsion polymerizations?
44. Which will have the higher specific gravity (density): (a) PVC or (b) PVDC?
45. Compare the properties of PMMA and glass.
46. Why is there a concern over the use of plasticizers?

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Each of these types of copolymers offers different physical properties for a particular copolymer combination. It is interesting to note that block copolymers may be produced from one monomer only if the arrangement around the chiral carbon atom changes sequentially. These copolymers are called “**stereoblock**” copolymers.

8.1 KINETICS OF COPOLYMERIZATION

Because of a difference in the reactivity of monomers, expressed as reactivity ratios (r), the composition of the copolymer (n) may be different from that of the reactant mixture or feed (x). When x equals n (Equation 8.5), the product is said to be an “**azeotropic copolymer**.”

In the early 1930s, Nobel Laureate Staudinger analyzed the product obtained from the copolymerization of equimolar quantities of vinyl chloride (VC) and vinyl acetate (VAc). He found that the first product produced was high in VC, but as the composition of the reactant mixture changed because of a preferential depletion of VC, the product was becoming higher in VAc. This phenomenon is called the “**composition drift**.”

Wall studied the composition drift and derived what is now called the Wall equation where n was equal to rx when the reactivity ratio r was equal to the ratio of the propagation rate constants. Thus, r was the slope of the line obtained when the ratio of monomers in the copolymer (M_1/M_2) was plotted against the ratio of monomers in the feed (m_1/m_2). The Wall equation (8.5) is not general.

$$(8.5) \quad n = \frac{M_1}{M_2} = r \left(\frac{m_1}{m_2} \right) = rx$$

The copolymer equation that is now accepted was developed in the late 1930s by a group of investigators including Wall, Dostal, Lewis, Alfrey, Simha, and Mayo. These workers considered the four possible extension reactions when monomers M_1 and M_2 were present in the feed. As shown in the following text, two of these reactions are homopolymerizations or self-propagating steps (8.6 and 8.8), and the other two are heteropolymerizations or cross-propagating steps (8.7 and 8.9). The ratios of the propagating rate constants are expressed as “**monomer reactivity ratios**” (or simply reactivity ratios), where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. M_1^\bullet and M_2^\bullet are used as symbols for the macroradicals with M_1^\bullet and M_2^\bullet terminal groups, respectively.

	Reaction	Rate constant	Rate expression
(8.6)	$M_1^\bullet + M_1 \rightarrow M_1M_1^\bullet$	k_{11}	$R_{11} = k_{11} [M_1^\bullet] [M_1]$
(8.7)	$M_1^\bullet + M_2 \rightarrow M_1M_2^\bullet$	k_{12}	$R_{12} = k_{12} [M_1^\bullet] [M_2]$
(8.8)	$M_2^\bullet + M_2 \rightarrow M_2M_2^\bullet$	k_{22}	$R_{22} = k_{22} [M_2^\bullet] [M_2]$
(8.9)	$M_2^\bullet + M_1 \rightarrow M_2M_1^\bullet$	k_{21}	$R_{21} = k_{21} [M_2^\bullet] [M_1]$

Experimentally, it is found that the specific rate constants for these various reaction steps are essentially independent of chain length, with the rate of monomer addition primarily dependent only on the adding monomer unit and the growing end. Thus, the four reactions between two comonomers can be described using only these four equations.

As is the case with the other chain processes, determining the concentration of the active species is difficult so that expressions that do not contain the concentration of the active species are derived. The change in monomer concentration, that is, the rate of addition of monomer to growing copolymer chains, is described in the following:

$$(8.10) \quad \text{Disappearance of } M_1 : -\frac{d[M_1]}{dt} = k_{11} [M_1^\bullet] [M_1] + k_{12} [M_2^\bullet] [M_1]$$

$$(8.11) \quad \text{Disappearance of } M_2 : -\frac{d[M_2]}{dt} = k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2]$$

Since it is experimentally observed that the number of growing chains remains approximately constant throughout the duration of most copolymerizations (i.e., a steady state in the number of growing chains), the concentrations of M_1^\bullet and M_2^\bullet are constant, and the rate of conversion of M_1^\bullet to M_2^\bullet is equal to the conversion of M_2^\bullet to M_1^\bullet . Solving for M_1^\bullet gives

$$(8.12) \quad [M_1^\bullet] = \frac{k_{21}[M_2^\bullet][M_1]}{k_{12}[M_2]}$$

The ratio of disappearance of monomers M_1/M_2 is described by Equation 8.13 from Equations 8.10 and 8.11. Remember that this is also the average composition of the growing chains and resulting polymer.

$$(8.13) \quad \frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1]}{k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2]} = \frac{[M_1](k_{11}[M_1^\bullet] + k_{21}[M_2^\bullet])}{[M_2](k_{22}[M_2^\bullet] + k_{12}[M_1^\bullet])}$$

Substitution of $[M_1^\bullet]$ into Equation 8.13 gives

$$(8.14) \quad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{(k_{11}k_{21}[M_2^\bullet][M_1]/k_{12}[M_2]) + k_{21}[M_2^\bullet]}{(k_{12}k_{21}[M_2^\bullet][M_1]/k_{21}[M_2]) + k_{22}[M_2^\bullet]} \right\}$$

Division by k_{12} and cancellation of the appropriate k 's gives

$$(8.15) \quad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{(k_{11}[M_2^\bullet][M_1]/k_{12}[M_2]) + [M_2^\bullet]}{([M_2^\bullet][M_1]/[M_2]) + k_{22}[M_2^\bullet]/k_{21}} \right\}$$

Substitution of $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and cancellation of $[M_2^\bullet]$ gives

$$(8.16) \quad \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{(r_1[M_1]/[M_2]) + 1}{([M_1]/[M_2]) + r_2} \right\}$$

Multiplication by $[M_2]$ gives what are generally referred to as the “[copolymerization equations](#)” (Equations 8.17 and 8.19), which give the copolymer composition without the need to know any free radical concentration and which give the composition of the growing polymer as a function of monomer feed (8.19).

$$(8.17) \quad n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

This equation (8.17) is also presented in another form that allows greater ease of seeing the relationship between the monomer feed, x , and copolymer composition. This is achieved by the following steps:

Multiplying through by $[M_1]$ and $[M_2]$ gives

$$(8.18) \quad n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1] r_1[M_1] + [M_1][M_2]}{[M_2][M_1] + [M_2]r_2[M_2]}$$

Then divide both the top and bottom by $[M_1]$ $[M_2]$ to get the second form (8.19) of the copolymerization equation but in terms of the composition of the feed (x) on the composition of the copolymer (n) as shown in the following:

$$(8.19) \quad n = \frac{d[M_1]}{d[M_2]} = \frac{r_1 ([M_1]/[M_2]) + 1}{r_2 ([M_2]/[M_1]) + 1} = \frac{r_1 x + 1}{r_2/x + 1}$$

The reactivity ratios are determined by an analysis of the change in the composition of the feed during the early stages of polymerization. Typical free radical chain copolymerization reactivity ratios are given in Table 8.1.

The copolymer composition and type can be predicted by looking at the values of r_1 and r_2 . If the value of r_1 is greater than 1, then M_1 tends to react with itself producing homopolymer

TABLE 8.1 Typical Free Radical Chain Copolymerization Reactivity Ratios at 60°C Unless Otherwise Noted

M_1	M_2	r_1	r_2	$r_1 r_2$
Acrylamide	Acrylic acid	1.38	0.36	0.5
	Methyl acrylate	1.30	0.05	0.07
	Vinylidene chloride	4.9	0.15	0.74
Acrylic acid	Acrylonitrile (50°C)	1.15	0.35	0.40
	Styrene	0.25	0.50	0.04
	Vinyl acetate (70°C)	2	0.1	0.2
Acrylonitrile	Butadiene	0.25	0.33	0.08
	Ethyl acetate (50°C)	1.17	0.67	0.78
	Maleic anhydride	6	0	0
	Methyl methacrylate	0.13	1.16	0.15
	Styrene	0.04	0.41	0.16
	Vinyl acetate	4	0.06	0.24
	Vinyl chloride	3.3	0.02	0.07
Butadiene	Methyl methacrylate	0.70	0.32	0.22
	Styrene	1.4	0.78	1.1
Isoprene	Styrene	2	0.44	0.88
Maleic anhydride	Methyl acrylate	0	2.5	0
	Methyl methacrylate	0.03	3.5	0.11
	Styrene	0	0.02	0
	Vinyl acetate (70°C)	0.003	0.055	0.0002
Methyl acrylate	Acrylonitrile	0.67	1.3	0.84
	Styrene	0.18	0.75	0.14
	Vinyl acetate	9.0	0.10	0.90
	Vinyl chloride	5	0	0
Methyl methacrylate	Styrene	0.50	0.50	0.25
	Vinyl acetate	20	0.015	0.3
	Vinyl chloride	12.5	0	0
Styrene	<i>p</i> -Chlorostyrene	0.74	1.03	0.76
	<i>p</i> -Methoxystyrene	1.2	0.82	0.95
	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	2-Vinylpyridine	0.56	0.9	0.50
Vinyl acetate	Vinyl chloride	0.23	1.7	0.39
	Vinyl laurate	1.4	0.7	0.98
Vinyl chloride	Dimethyl maleate	0.77	0.009	0.007

Source: Data from Brandrup and Immergut (1975).

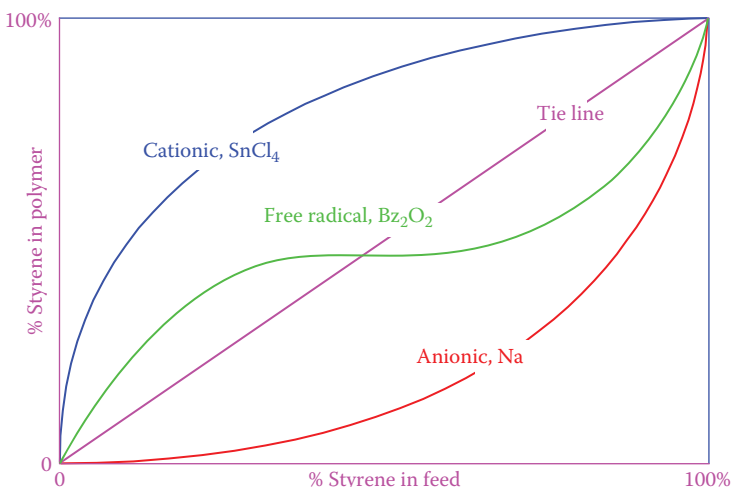


FIGURE 8.1 Instantaneous copolymer composition as a function of monomer composition and initiator employed for the comonomer system of styrene and methyl methacrylate using different modes of initiation. (From Landler, Y., *Comptes Rendus*, 230, 539, 1950.)

units, or block copolymers in M_1 . Preference for reaction with the unlike monomer occurs when r_1 is less than 1. When r_1 and r_2 are approximately equal to 1, the conditions are said to be ideal, with a random (not alternating) copolymer produced, in accordance with the Wall equation. Thus, a random copolymer (ideal copolymer) would be produced when chlorotrifluoroethylene is copolymerized with tetrafluoroethylene (Table 8.1).

The resonance stability of the macroradical is an important factor in polymer propagation. Thus, for free radical polymerization, a conjugated monomer such as styrene is at least 30 times as apt to form a resonance-stabilized macroradical as VAc, resulting in a copolymer being rich in styrene-derived units when these two are copolymerized.

Strongly electrophilic or nucleophilic monomers will polymerize exclusively by anionic or cationic mechanisms. However, monomers that are neither strongly electrophilic nor nucleophilic generally polymerize by ionic and free radical processes. The contrast between anionic, cationic, and free radical methods of addition copolymerization is clearly illustrated by the results of copolymerization utilizing the three modes of initiation (Figure 8.1). Such results illustrate the variations of reactivities and copolymer composition that are possible from employing the different initiation modes. The free radical “tieline” resides near the middle since free radical polymerizations are less dependent on the electronic nature of the comonomers relative to the ionic modes of chain propagation.

As noted before, the copolymerization can be controlled by control of the monomer feed in accordance of equations such as (8.17) and (8.19).

8.2 THE Q-e SCHEME

A useful scheme for predicting r_1 and r_2 values for free radical copolymerizations was developed by Alfrey and Price in 1947. The Alfrey–Price Q–e scheme is similar to the Hammett equation approach except that it is not primarily limited to substituted aromatic compounds. In the semiempirical Q–e scheme, the reactivities or resonance effects of the monomers and macroradicals are evaluated empirically by Q and P values. The polar properties of both monomers and macroradicals are designated by arbitrary “e” values. Thus, as shown in Table 8.2, Q_1 and Q_2 are related to the reactivity, and e_1 and e_2 are related to the polarity of monomers M_1 and M_2 , respectively. Styrene is assigned the Q value of 1 and an e value of -0.80 . Higher Q values indicate greater resonance stability or reactivity, and higher e values (less negative) indicate greater electron-withdrawing power of the α -substituents on the vinyl monomer (in comparison to the phenyl substituent in styrene).

TABLE 8.2 Typical *Q* and *e* Values for Monomers

Monomer	<i>Q</i>	<i>e</i>
Benzyl methacrylate	3.64	0.36
Methacrylic acid	2.34	0.65
2-Fluoro-1,3-butadiene	2.08	−0.43
<i>p</i> -Cyanostyrene	1.86	−0.21
<i>p</i> -Nitrostyrene	1.63	0.39
2,5-Dichlorostyrene	1.60	0.09
Methacrylamide	1.46	2.24
<i>p</i> -Methoxystyrene	1.36	−1.11
2-Vinylpyridine	1.30	−0.50
<i>p</i> -Methylstyrene	1.27	−0.98
Methacrylonitrile	1.12	0.81
<i>p</i> -Bromostyrene	1.04	−0.32
Styrene	1.00	−0.80
<i>m</i> -Methylstyrene	0.91	−0.72
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Methyl acrylate	0.42	0.60
Vinylidene chloride	0.23	0.36
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	−0.22

8.3 COMMERCIAL COPOLYMERS

One of the first commercial copolymers, introduced in 1928, was made of VC (87%) and VAc (13%) (Vinylite). Because the presence of the VAc mers disrupted the regular structure of PVC, the copolymer was more flexible and more soluble than PVC itself.

Copolymers of VC and vinylidene chloride were introduced in the 1930s. The copolymer with a very high VC content is used as a plastic film (Pliovic), and the copolymer with a high vinylidene chloride content is used as a film and filament (Saran).

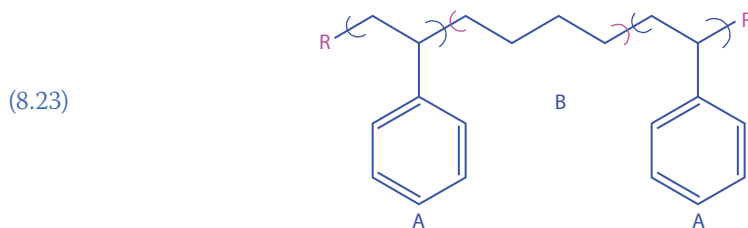
Polybutadiene, produced in emulsion polymerization, is not useful as an elastomer. However, copolymers with styrene (SBR) and acrylonitrile (Buna-N) are widely used as elastomers.

Ethylene-propylene copolymers (EPMs) show good resistance to ozone, heat, and oxygen and are used in blends to make today's external automotive panels. Two general types of EPMs are commercially available. EPMs are saturated and require vulcanization if used as a rubber. They are used in a variety of automotive applications including as body and chassis parts, bumpers, radiator and heater hoses, seals, mats, and weather strips. EPMs are produced using Ziegler–Natta catalysts.

The second type of EPM is the ethylene-propylene-diene terpolymers (EPDMs). These are made by polymerizing ethylene, propylene, and a small amount (3–10 mol%) of nonconjugated diolefine employing Ziegler–Natta catalysts. The side chains allow vulcanization with sulfur. They are employed in the production of appliance parts, wire and cable insulation, coated fabrics, gaskets, hoses, seals, and high-impact polypropylene (PP).

8.4 BLOCK COPOLYMERS

While block copolymers do not occur naturally, synthetic block copolymers have been prepared by all known classical polymerization techniques. The first commercial block copolymer was a surfactant (Pluronic) prepared by the addition of propylene oxide to polycarbanions



Today, new copolymers are making use of the hard–soft block strategy where the hard segment is a block portion as PE that readily crystallizes forming a physical cross-link. The soft segment consists of blocks formed from α -olefins such as 1-butene, 1-hexene, and 1-octane where the substituted alkane-arm discourages crystallization.

8.5 GRAFT COPOLYMERS

The major difference between block and graft copolymers is the position of the second kind of unit. Thus, information that applies to block copolymers can often be applied to graft copolymers. So domains where physical cross-linking occurs via crystallization can occur in either block components or within graft copolymers where the necessary symmetry occurs.

Graft copolymers of nylon, protein, cellulose, or starch, or copolymers or vinyl alcohol have been prepared by reaction of ethylene oxide with these polymers. Graft copolymers are also produced when styrene is polymerized by Lewis acids in the presence of poly-*p*-methoxystyrene. The Merrifield synthesis of polypeptides is also based on graft copolymers formed from chloromethylated polystyrene (PS). Thus, the variety of graft copolymers is large.

The most widely used graft copolymer is the styrene-unsaturated polyester copolymer. This copolymer, which is usually reinforced by fibrous glass, is prepared by the free radical chain polymerization of a styrene solution of an unsaturated polyester.

The graft copolymers of acrylamide, acrylic acid, and cellulose or starch are used as water absorbents and in enhanced oil recovery systems.

8.6 ELASTOMERS

8.6.1 GENERAL

Elastomers typically contain chemical and/or physical cross-links. While there are thermoplastic elastomers such as SBS and block copolymers, most elastomers are thermosets. Elastomers are characterized by a disorganized (high-entropy) structure in the resting or nonstressed state. Application of stress is accompanied by a ready distortion requiring (relative to plastics and fibers) little stress to effect the distortion. This distortion brings about an aligning of the chains forming a structure with greater order. The driving force for such a material to return to its original shape is largely a return to the original less organized state. While entropy is the primary driving force for elastomers to return to the original resting state, the cross-links allow the material to return to its original shape giving the materials a type of memory. Materials that allow easy distortion generally have minimal interactions between the same or different chains. This qualification is fulfilled by materials that do not bond through the use of dipolar (or polar) or hydrogen bonding. Thus, the intermolecular and intramolecular forces of attraction are small relative to those present in fibers and plastics. Hydrocarbon-intense polymers are examples of materials that meet this qualification. Production generally requires the initial production of linear polymers, followed by the insertion of cross-links through a process called vulcanization or curing. Addition of fillers and other additives such as carbon black also is typical. Table 8.3 contains a listing of important elastomers.

The introduction of cross-links to inhibit chain slippage was discovered by Goodyear in 1839. He accomplished this through addition of sulfur to natural rubber. Shortly after this, an

TABLE 8.3 Common Elastomers and Their Uses

Common Name (Chemical Composition)	Abbreviation	Uses and Properties
Acrylonitrile–butadiene–styrene (terpolymer)	ABS	Oil hoses, fuel tanks, gaskets, pipe and fittings, appliance and automotive housings; good resistance to oils and gas
Butadiene rubber	BR	Tire tread, hose, belts; very low hysteresis, high rebound
Butyl rubber (from isobutene and 0.5%–3% isoprene)	IIR	Inner tubes, cable sheathing, tank liners, roofing, seals, coated fabrics; very low rebound, high hysteresis
Chloroprene rubber (polychloroprene)	CR	Wire and cable insulation, hose footwear, mechanical automotive products; good resistance to oil and fire, good weatherability
Epichlorohydrin (epoxy copolymers)		Seals, gaskets, wire and cable insulation; good resistance to chemicals
Ethylene–propylene rubbers (random copolymers with 60%–80% ethylene)	EP or EPM	Cable insulation, window strips; outstanding insulative properties
Ethylene–propylene–diene (random terpolymers)	EPDM	Good resistance to weathering, resistant to ozone attack
Fluoroelastomers (fluorine-containing copolymers)		Wire and cable insulation, aerospace applications; outstanding resistance to continuous exposure to high temperatures, chemicals, and fluids
Ionomers (largely copolymers of ethylene and acid-containing monomers with metal ions)		Golf ball covers, shoe soles, weather stripping; tough, flame resistant, good clarity, good electrical properties, abrasion resistant
Natural rubber (polyisoprene)	NR	General-purpose tires, bushings, and couplings, seals, footwear, belting; good resilience
Nitrile rubber (random copolymer of butadiene and acrylonitrile)	NBR	Seals, automotive parts that are in contact with oils and gas, footwear, hose; outstanding resistance to oils and gas, little swelling in organic liquids
Polysulfide		Adhesive, sealants, hose binders; outstanding resistance to oil and organic solvents
Polyurethanes		Sealing and joining, printing rollers, fibers, industrial tires, footwear, wire and cable coverings
Silicones (generally polydimethylsiloxane)		Medical applications, flexible molds, gaskets, seals; extreme use temperature range
Styrene–butadiene rubber (random copolymer)	SBR	Tire tread, footwear, wire and cable covering, adhesives; high hysteresis

accelerator, zinc (II) oxide, was used to speed up the process. Other additives were discovered often through observation and trial and error so that today's elastomers often have a number of important additives that allow them to perform demanding tasks.

About 1915, Mote found that a superior abrasion-resistant elastomer was produced through the use of carbon black (Chapter 10). Today, it is recognized that factors such as surface area, structure, and aggregate size are important features in the production of superior elastomers. For instance, high surface areas (small particle size) increase the reinforcement and consequently the tensile strength and improve the resistance to tearing and abrasion. Large aggregates give elastomers improved strength before curing, high modulus, and an improved extrusion behavior.

Rubbers typically have low hysteresis. “**Hysteresis**” is a measure of the energy absorbed when the elastomer is deformed. A rubber that absorbs a great amount of energy as it is deformed (such as a tire hitting bumps on the roadway) is said to have a high hysteresis. The absorbed energy is equivalent to the reciprocal of resilience such that a material with a low hysteresis has a high resilience. Rubbers with a particularly high hysteresis are used where heat buildup is desirable such as in tires to give the tread a better grip on the road and the tire a smoother ride.

Typical thermosetting elastomers are difficult to recycle because their cross-linking prevents them from being easily solubilized and reformed through application of pressure and heat.

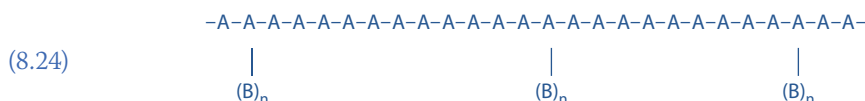
Recycling can be accomplished through the partializing (grinding into small particles) of the elastomeric material followed by a softening-up by application of a suitable liquid and/or heat and finally addition of a binder that physically or chemically allows the particles to bind together in the desired shape.

8.6.2 THERMOPLASTIC ELASTOMERS

A number of thermoplastic elastomers have been developed since the mid-1960s. The initial thermoplastic elastomers were derived from plasticized PVC and are called *plastisols*. *Plastisols* are formed from the fusing together of PVC with a compatible plasticizer through heating. The plasticizer acts to lower the T_g to below room temperature. Conceptually, this can be thought of as the plasticizer acting to put additional distance between the PVC chains, thus lowering the inter- and intrachain forces as well as helping solubilize chain segments. The resulting materials are used in a number of areas including construction of boot soles.

The hard–soft segment scenario is utilized in the formation of a number of industrially important thermoplastic elastomers. Thermoplastic elastomers contain two or more distinct phases and their properties depend on these phases being intimately mixed and small. These phases may be chemically or physically connected. In order that the material be a thermoplastic elastomer, at least one phase must be soft or flexible under the operating conditions and at least one phase is hard with the hard phase(s) becoming soft (or fluid) at higher temperatures. Often the hard segments or phases are crystalline thermoplastics, while the soft segments or phases are amorphous. In continuous chains containing blocks of hard and soft segments, the molecular arrangement normally contains crystalline regions where there is sufficient length in the hard segment to form the crystalline regions or phases where the soft segments form amorphous regions.

Such hard–soft scenarios can also be achieved through employing grafts where the pendant group typically acts as the hard segment with the backbone acting as the soft segment. The following (8.24) is a representation of a typical graft copolymer chain. In order for an effective network to be formed, each “A” chain needs to have at least two “B” grafts to allow for formation of a continuous interlinked network. While there has been a lot of research done with such graft materials, they have not yet become very important commercially.



Thermoplastic elastomers can also be achieved through physical mixing of hard and soft segments. These are fine dispersions of a hard thermoplastic polymer and an elastomer. The two materials generally form interdispersed co-continuous phases. Often the physical combining is achieved through intense mechanical mixing, but in some cases, such as with PP and EPDMs, the effect of blending is achieved through polymerizing the finely dispersed elastomer phase (EPM) simultaneously with the hard PP.

At times the phases are cross-linked during the mechanical mixing. This process is referred to as “dynamic vulcanization” and produces a finely dispersed discontinuous cross-linked elastomer phase. The products are referred to as thermoplastic vulcanizates or dynamic vulcanizates. The products of this process have an insoluble elastomer phase giving the material greater oil and solvent resistance. The cross-linking also reduces or eliminates the flow of this phase at high temperatures and/or under high stress. This allows the material better resistance to compression set.

8.6.3 SBR COPOLYMERS

SBS block copolymers differ structurally from the random copolymer of styrene and butadiene (SBR). Because styrene and butadiene blocks are incompatible, they form separate phases joined at the junctions where the various blocks are connected. This gives an elastomeric material where the butadiene blocks form the soft segments and the styrene blocks form hard blocks.

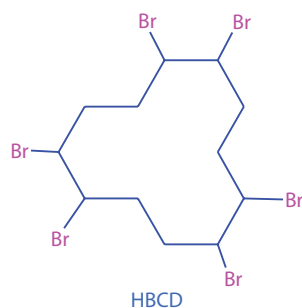
The block copolymer made from connecting blocks of PS with blocks of polybutadiene illustrates another use of soft and rigid or hard domains in thermoplastic elastomers. The PS blocks give rigidity to the polymer while the polybutadiene blocks act as the soft or flexible portion. The PS portions also form semicrystalline domains that add to the strength of the copolymer, and these domains also act as “physical cross-links” allowing the soft portions to respond in an “elastomeric” manner, while the semicrystalline domains give the material the “elastomeric” memory. The polybutadiene blocks act as the continuous phase while the PS blocks act as the discontinuous phase. Heating the material above the T_m of the PS domains allows whole chain mobility allowing processability of the virgin material and subsequent reprocessability of used material. Upon cooling, the rigid domains reform. Block PS-polybutadiene copolymers are used in the soles of many of the athletic shoes.

8.6.4 SALES AND FLAMMABILITY

Worldwide sales of thermoplastic elastomers are on the order of one and a half million tons with a value of about \$5 billion.

One of the ongoing problems involves the use of flame retardants that are not toxic. Many of the present flame retardants are based on hexabromocyclododecane (HBCD) (8.25), which is widely used to help PS foam insulation meet fire safety codes. Burning is complex but is believed to include the formation of oxygen-derived free radicals. HBCD, and other bromine-containing flame retardants, trap oxygen-produced free radicals preventing them from continuing to propagate the burning. But HBCD releases various toxins in flames. DOW is developing a polymeric substituent. One major argument for polymeric flame retardants is the idea that as the polymeric flame retardants decompose, they will break into fragments 1000 Da long or longer, which are believed too large to penetrate cell walls; thus they should not bioaccumulate or be toxic to us. The polymer currently being considered is a block copolymer of PS and polypolybutadiene. The polybutadiene block is brominated providing the flame resistance. Further, as the copolymer disintegrates, the PS block provides styrene fragments that produce radical traps assisting in limiting further degradation.

(8.25)



8.7 BLENDS

8.7.1 GENERAL

There is an ongoing search for new materials and materials that exhibit needed properties. Blends are one of the major avenues of achieving these new materials without actually synthesizing new polymers. “Polymer blends” are physical mixtures of two or more polymers though sometimes the various phases are chemically bonded together. These blended mixtures may offer distinct properties, one set of properties related to one member of the blend and another set of properties related to the second member of the blend. The blended mixtures may also offer some averaging of properties. The property mix of polymeric blends is dependent on a number of factors, one of the major being the miscibility of the polymers in one another. This miscibility is in turn dependent on the nature of the polymers composing the blend and the amount of each component in the blend. Here polymer blends will be divided into miscible and immiscible polymer blends.

The extent of mixing is related to time since mixing requires sufficient time to allow the polymer chains to mix. Thus, for miscible blends, particular structures can be “frozen-in” by rapid cooling when the desired mixing is achieved. Here, micelles of particular structures can cause the mixture to perform in one manner governed by the particular grouping that may not occur if more total mixing occurs.

Miscibility/immiscibility can be described in simple thermodynamic terms as follows (8.26), at constant temperature. Mixing occurs if the free energy of mixing is negative.

$$(8.26) \quad \Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}}$$

Mixing is exactly analogous with polymer solubility. The driving force for mixing and solubility is the entropy or random-related term. The entropy-related term must overcome the opposing enthalpy energy term. In a more complete treatment, temperature and volume fraction must be considered.

8.7.2 IMMISCIBLE BLENDS

Immiscible combinations are all about us. Oil and water is an immiscible combination: as is the lava in the so-called lava lamps and chicken broth in chicken soup. Immiscible blends are actually a miss naming at the molecular level since they are not truly mixed together. But at the macro-level, they appear mixed, so the name immiscible blends.

Immiscible blends are said to be phase separated, that is, there are different phases mixed together. Both phases are solid in behavior.

Because PS is brittle with little impact resistance under normal operating conditions, early work was done to impart impact resistance. The best known material from this work is called high-impact polystyrene or HIPS. HIPS is produced by dispersing small particles of butadiene rubber with the styrene monomer. Bulk or mass polymerization of the styrene is begun producing what is referred to as prepolymerization material. During the prepolymerization stage, styrene begins to polymerize with itself forming droplets of PS with phase separation. When nearly equal phase volumes of polybutadiene rubber particles and PS are obtained, phase inversion occurs and the droplets of PS act as the continuous phase within which the butadiene rubber particles are dispersed. The completion of the polymerization generally occurs employing either bulk or aqueous suspension conditions.

Most HIPS has about 4%–12% polybutadiene in it so that HIPS is mainly a PS-intense material. The polymerization process is unusual in that both a matrix composition of PS and polybutadienes is formed as well as a graft between the growing PS onto the polybutadiene is formed. Grafting provides the needed compatibility between the matrix phase and the rubber phase. Grafting is also important in determining the structure and size of rubber particles that are formed. The grafting reaction occurs primarily by hydrogen abstraction from the polybutadiene backbone by growing either PS chains or alkoxy radicals if peroxide initiators are employed.

HIPS is an immiscible blend that is used in many applications and used to be employed as the material for some of the large transport truck of the bumpers. The PS portion is strong and inflexible, while the polybutadiene particles are flexible allowing an impact to be distributed over a larger area. The polybutadiene rubbery portion allows the bumper to bend and indent and protects the PS from fracturing while the PS phase resists further deformation. This combination gives a strong flexible material.

8.7.3 IMMISCIBLE BLENDS: REMAINDER OF THE SECTION ON IMMISCIBLE BLENDS

In general, the morphology on a molecular level varies with the fraction of each component in the mixture. In general terms, we can talk about a continuous and discontinuous phase. For a combination of polymers A and B, such as PS and polybutadiene, at low amounts of A, polymer A will typically act as a discontinuous phase surrounded by B. Thus, at low amounts of PS, the PS congregates as small particles in a “sea” or continuous phase of B, the polybutadiene. As the

fraction of polymer A increases, the spheres eventually become so large as to join together forming a continuous phase, and so two continuous phases are present. As the fraction of A continues to increase, polymer B becomes the discontinuous phase, being surrounded by the continuous phase polymer A.

The discontinuous phase generally takes the rough shape of a sphere to minimize surface area exposure to the other phase. The size of the spheres influences the overall properties and varies with concentration. In general, because of the affinity of polymer chains, spheres tend to grow. Larger sphere sizes are promoted because they give less relative contact area with the other phase.

As noted earlier, immiscible blends can exhibit different properties. If the domains are of sufficient size, they may exhibit their own T_g and T_m values. Many commercially used immiscible blends have two separate T_g and/or T_m values.

Blends can also offer variable physical properties as already noted for high-impact polystyrene (HIPS). Consider a blend of polymer PS and butadiene where butadiene is the major component. PS is the stronger material with the blend weaker than PS itself. In some cases, the blend can be stronger than the individual polymers. Heat and pressure can result in the change of the discontinuous phase becoming flatten out when pressed against a mold. The spheres can also be caused to elongate forming rodlike structures with the resulting structure similar to composites where the rodlike structures strengthen the overall structure.

The strength can also be increased by using about the same amounts of the two polymers so that they form two continuous phases. Here, both phases can assist the blend to be strong. Another approach is to use compatibilizers. *Compatibilizers* are materials that help bind together the phases allowing stress/strain to be shared between the two phases. Many compatibilizers are block copolymers where one block is derived from polymers of one phase and the second block is composed of units derived from polymers of the second phase. The two blocks get “locked” into the structures of the like phases and thus serve to connect the two phases.

Graft copolymers are also used as compatibilizers to tie together different phases. HIPS contains PS grafted onto polybutadiene backbones. This allows stress/strain to be transferred from the PS to the polybutadiene phase transferring energy that might break the brittle PS to the more flexible polybutadiene phase. That is why HIPS is stronger than PS itself.

Compatibilizers also act to modify the tendency to form large spheres. The formation of large spheres is a result of the two polymer components trying to segregate. The compatibilizer causes the two phases to come together minimizing the tendency to form large spheres. For instance, for a mixture of 20:80 PS/polybutadiene the sphere size is about 5–10 μm , whereas addition of about 9% PS/PE (PE is enough like polybutadiene to be incorporated into the polybutadiene phases) block copolymer results in PS spheres of about 1 μm . This increases the interface between the two phases resulting in better mechanical properties because stress/strain can be more effectively transferred from one phase to the other.

8.7.4 MISCIBLE BLENDS

Miscible blends are not as easy to achieve as immiscible blends. As noted earlier, entropy is the major driving force in causing materials to mix. Increases in randomness are not easily achieved so that immiscible blends are often more easily formed. To make matters worse, for amorphous polymers, the amount of disorder in the unmixed polymer is often higher than for blends that tend to arrange the polymer chains in a more ordered fashion.

Sometimes special attractions allow polymers to mix. This is true for the mixture of PS and poly(phenylene oxide) (PPO), where the interaction between the phenyl groups allows the miscibility of the two polymers. For many combinations, such preferential associations are not present.

Another approach is the use of copolymers. There are a number of variations to this. In some situations, polymer–copolymer combinations are used where the adage “the enemy of my enemy is my friend” comes into play. Thus, the random copolymer of styrene and acrylonitrile forms a miscible blend with poly(methyl methacrylate) (PMMA). The copolymer is composed of nonpolar styrene units and polar acrylonitrile units that are incompatible with one another. These units will blend with PMMA in order to avoid one another.

Generally, miscible blends will have properties somewhere between those of the unblended polymers. These properties will be dependent on the ratio of the two polymers and this ratio is often used to obtain a particular property. These properties include mechanical, chemical, thermal, and weathering. For instance, PPO is thermally stable with a high T_g , about 210°C. While this is good for some applications, it is considered too high for easy processing. Thus, PS, with a T_g of about 100°C, is added to allow a lower processing temperature. Noryl is PPO blended with a second polymer, which is generally PS or HIPS. Noryl is used in the construction of internal appliance components, brackets and structural components in office products, large computer and printer housings, automotive wheel covers, and high-tolerance electrical switch boxes and connectors.

Another approach is to use copolymers where the structures of the copolymer are similar to that of the other phase. This is what occurs for PE and copolymers of ethylene and propylene.

Industrial companies have long-term strategies. For example, Exxon (now ExxonMobil) is the third largest chemical company in the United States. Some time ago, they made the decision to emphasize the ethylene and propylene monomers that are obtained from the petrochemical interests of ExxonMobil. Thus, ExxonMobil has a research emphasis on the commercialization of products from these monomers. The major materials made from ethylene and propylene are polymeric, either homopolymers or copolymers. Efforts include developing catalysts that allow the formation of polymeric materials from the ethylene and propylene monomers and the use of these catalysts to synthesize polymeric materials that have varying properties allowing their application in different marketplaces in society.

A driving force for conversion of gasoline to polymeric materials is increased value in the products made from the polymers. The general trail is gasoline → ethylene, propylene monomers → raw polymers, and copolymers → finished products.

As noted previously, one major use of HIPS was in automotive bumpers. These have been largely replaced by another blend, but here it is a miscible blend of PE and PP. HIPS bumpers have a more rubbery feel to them while the PE–PP materials are more plastic in their behavior and feel. These PE and PP intense plastics are made not only into automotive bumpers (Picture 8.1) but also as side and bottom panels. There are several processes employed to produce the raw materials used in the production of these automotive parts. One process developed by Exxon begins with the production of PP using a catalyst developed by Exxon. This catalyst system produces isotactic stereoregular polypropylene (iPP) that is stronger and denser than atactic nonstereoregular



PICTURE 8.1 Plastic bumpers synthesized as miscible blends of polyethylene and polyethylene/polypropylene.

polypropylene (aPP). At some time during this polymerization, some of the liquid PP monomer is removed and ethylene monomer is added to the mix. Because of the continued presence of the catalyst that can also polymerize the ethylene monomer, copolymer containing ethylene and iPP units is produced. This product can be roughly pictured as being formed from iPP particles that have unreacted propylene monomer removed creating open-celled spongelike particles. These iPP particles then become impregnated with ethylene monomer eventually resulting in the formation of a copolymer that contains both iPP and PE units with an iPP outer shell. This product is eventually mixed with an ethylene (60%)-iPP (40%) copolymer giving a blended material that has two continuous phases with a final iPP content of 70%. It is this material that is used in molding the automotive bumpers and panels. The iPP units contribute stiffness and the PE units contribute flexibility to the overall product. The inner PE units in the impregnated particles allow stress to be rapidly distributed to the stiffer outer iPP shell. The closeness of structure between the two components, the iPP impregnated particles and the PE/iPP copolymer, allows miscible mixing of the two phases.

The actual conditions and concentrations and ratios of monomer were developed by research scientists such as Edward Kresge over a long period of time.

8.8 POLYMER MIXTURES: IPNs AND ALLOYS

Today there exist a number of polymer mixtures including blends noted in the previous section. Here we will briefly look at two more mixtures. A plastic or polymer alloy is a physical mixture of two or more polymers in a melt and is often structurally similar to blends; in fact the terms blends and alloys are sometimes used to describe the same materials. While some cross-linking may occur, such materials are generally not viewed as copolymers, though they are covered in this chapter along with blends and dendrites. Many alloys contain a matrix that is a mixture of polymer types with many of them containing acrylonitrile, butadiene, and styrene (ABS). ABS thermoplastics have a two-phase morphology consisting of elastic particles dispersed in a styrene-acrylonitrile copolymer matrix.

“Interpenetrating polymer networks” (IPNs) are described by Sperling to be an intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and/or cross-linked in the immediate presence of the other. This is similar to taking a sponge cake, soaking in it warm ice cream, and refreezing the ice cream, resulting in a dessert (or mess) that has both spongy and stiff portions. Such IPNs, grafts, blocks, and blends can offer synergistic properties that are being widely exploited.

8.9 DENDRITES

Along with the varying structures given in the previous sections, there exist other structurally complex molecules called dendrites developed by a number of scientists including Tomali and Frechet. These molecules can act as “spacers,” “ball bearings,” and building blocks for other structures. Usually, they are either wholly organic or they may contain metal atoms. They may or may not be copolymers depending on the particular synthetic route employed in their synthesis.

While some make a distinction between dendrimers and hyperbranched polymers, we will not do so here. In essence, hyperbranched polymers are formed under conditions that give a variety of related but different structures while dendrimers are often formed one step at a time giving a fairly homogeneous product.

Dendrites are highly branched, usually curved, structures. The name comes from the Greek name for tree “dendron.” Another term often associated with these structures is “dendrimers” describing the oligomeric nature of many dendrites. Because of the structure, dendrites can contain many terminal functional groups for each molecule that can be further reacted. Also, most dendrites contain “lots” of unoccupied space that can be used to “carry” drugs, fragrances, adhesives, diagnostic molecules, cosmetics, catalysts, herbicides, and other molecules.

The dendrite structure is determined largely by the “functionality” of the reactants. The dendrite, pictured in Figure 8.2a, can be considered as being derived from a tetrafunctional monomer

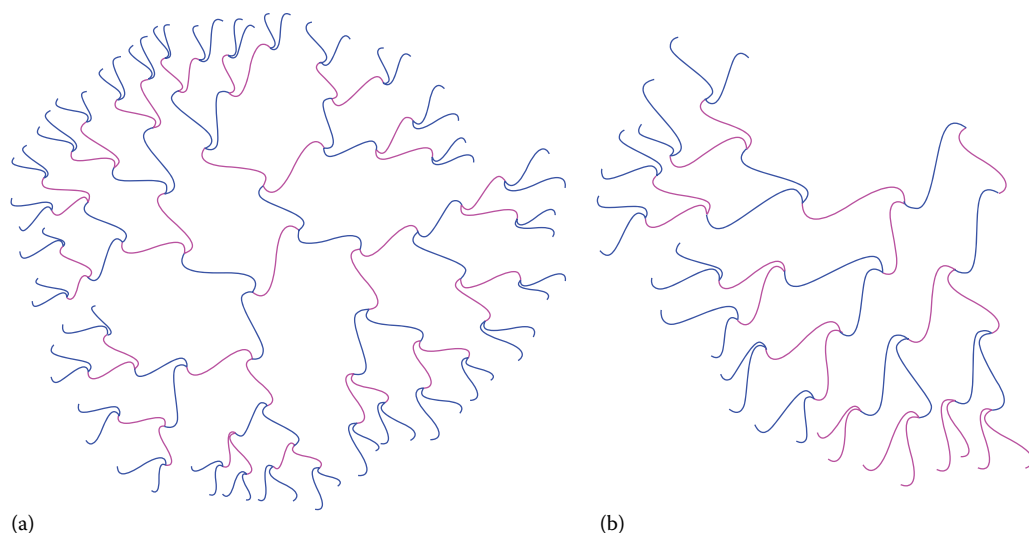


FIGURE 8.2 Dendrite structure derived from the reaction of 1,4-diaminobutane and acrylonitrile (a) and derived from “bent” difunctional reactants (b).

formed from the reaction of 1,4-diaminobutane and acrylonitrile. The resulting polypropylenimine dendrimer has terminal nitrile groups that can be further reacted extending the dendrimer or terminating further dendrimer formation. The resulting molecule is circular with some 3D structure. The dendrimer shown in Figure 8.2b is derived from difunctional reactants that are “bent” so as to encourage “fanlike” expansion rather than the typical linear growth.

Numerous approaches have been taken in the synthesis of dendrites or dendrimers. These approaches can be divided into two groupings. In divergent dendrimer growth, growth occurs outward from an inner core molecule. In convergent dendrimer growth, developed by Frechet and others, various parts of the ultimate dendrimer are separately synthesized and then they are brought together to form the final dendrimer.

The somewhat spherical shape of dendrimers gives them some different properties in comparison to more linear macromolecules. On a macroscopic level, dendrimers act as ball bearings rather than strings. In solution, viscosity increases as molecular weight increases for linear polymers. With dendrimers, viscosity also increases with molecular weight up to a point after which viscosity decreases as molecular weight continues to increase.

Dendrimers are being used as host molecules, catalysts, and self-assembling nanostructures; as analogs of proteins, enzymes, and viruses; and in analytical applications including in ion-exchange displacement chromatography and electrokinetic chromatography.

We are continuing to recognize that polymer shape is important in determining material property. Another group of structurally complex shapes is referred to as stars. There are a number of synthetic routes to star polymers. Fetters and coworkers developed a number of star polymers based on chlorosilanes. For instance, 3-, 12-, and 18-arm star polymers can be formed. These arms are now reacted with other reactants such as living PS or polybutadiene giving now the star polymers with the silicon-containing inner core and polymer outer core. Through control of the length of the grafted PS or other reactant, the size of the “star” can be controlled.

For dendrimers made using flexible arms, the core is mobile and depending upon the situation spends some time near the outer layer of the dendrimer sphere. On the other hand, stiff, rigid arms produce a dendrimer that “holds” its core within the interior of the dendrimer.

The term “generation” describes the number of times “arms” have been extended. The nature of each generation can be varied so that mixtures of steric requirements and hydrophobic/hydrophilic character can be introduced offering materials with varying structures and properties. By varying the hydrophobic and hydrophilic interactions and steric nature of the arms, secondary and tertiary structural preferences can be imposed on the dendrimer.

The dendrite structure can be used as a synthetic tool to craft a particular property into an overall structure.

8.10 IONOMERS

Ionomers are ion-containing copolymers typically containing over 90% (by number) ethylene units with the remaining being ion-containing units such as acrylic acid. These “ionic” sites are connected through metal atoms. Ionomers are often referred to as “**processable thermosets**.” They are thermosets because of the cross-linking introduced through the interaction of the ionic sites with metal ions. They are processable or exhibit thermoplastic behavior because they can be reformed through application of heat and pressure.

As with all polymers, the ultimate properties are dependent upon the various processing and synthetic procedures that the material is exposed to. This is especially true for ionomers where the location, amount, nature, and distribution of the metal sites strongly determine the properties. Many of the industrial ionomers are made where a significant fraction of the ionomer is unionied and where the metal-containing reactants are simply added to the preionomer followed by heating and agitation of the mixture. These products often offer superior properties to ionomers produced from fully dissolved preionomers.

Bonding sites are believed to be of two different grouping densities. One of these groupings involves only a few or individual bonding between the acid groups and the metal atoms. The second bonding type consists of large concentrations of acid groups with multiple metal atoms (clusters). This metal-acid group bonding (salt formation) constitutes sites of cross-linking. It is believed that the “processability” is a result of the combination of the movement of the ethylene units and the metal atoms acting as “ball bearings.” The “sliding” and “rolling” are believed to be a result of the metallic nature of the acid–metal atom bonding. (Remember that most metallic salts are believed to have a high degree of ionic, nondirectional bonding as compared with typical organic bonds where there exists a high amount of covalent, directional bonding.) Recently, Carraher and coworkers have shown that the ethylene portions alone are sufficient to allow ionomers to be processed through application of heat and pressure.

Ionomers are generally tough and offer good stiffness and abrasion resistance. They offer good visual clarity, high melt viscosities, superior tensile properties, and oil resistance and are flame retarders. They are used in the automotive industry in the formation of exterior trim and bumper pads, in the sporting goods industry as bowling pin coatings and golf ball covers (Picture 8.2), and in the manufacture of roller skate wheels and ski boots. Surlyn (DuPont; poly(ethylene-*co*-methacrylic acid)) is used in vacuum packaging for meats, in skin packaging for hardware and electronic items (such as seal layers and as foil coatings of multiwall bags), and in shoe soles.

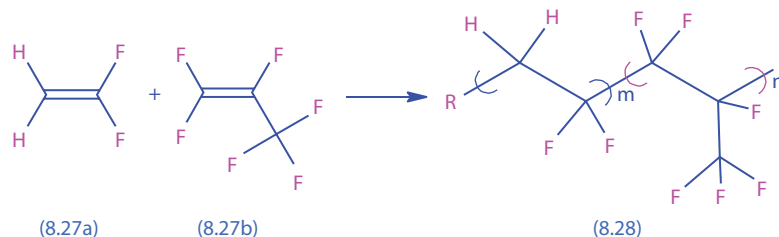


PICTURE 8.2 Golf ball with ionomer covering.

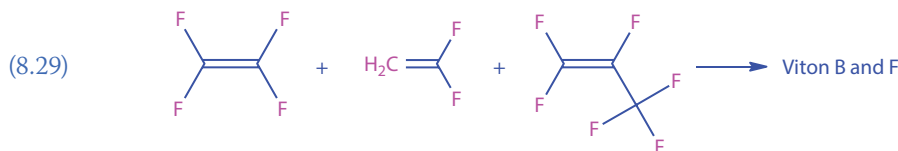
Sulfonated EPDM are formulated to form a number of rubbery products including adhesives for footwear and garden hoses and the formation of calendered sheets. Perfluorinated ionomers marketed as Nafion (DuPont) are used for membrane applications including chemical processing separations, spent acid regeneration, electrochemical fuel cells, ion-selective separations, and electrodialysis and in the production of chlorine. It is also employed as a “solid”-state catalyst in chemical synthesis and processing. Ionomers are also used in blends with other polymers.

8.11 FLUOROELASTOMERS

Fluoroelastomers are specialty copolymers containing a high amount of fluorine-containing units. These copolymers can be divided into three groups. Vinylidene difluoride (8.27) and hexafluoropropylene (8.28) form the copolymer Viton A (8.29). It is used as a general-purpose sealing material in the automotive industry and with aerospace fuels and lubricants.



Viton B (8.29) is a terpolymer produced from the polymerization of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene. It is used in power utility seals and gaskets.



Viton F is also a terpolymer of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene. It is used as seals for concentrated aqueous solutions of inorganic acids and for oxygenated automotive fuels. Finally, Viton Extreme is a copolymer of tetrafluoroethylene and propylene and the terpolymer of ethylene, tetrafluoroethylene, and perfluoromethylvinylether.

Viton O-rings are used in SCUBA diving when gas blends called Nitrox are employed. Viton has a low flammability even in the presence of high amounts of oxygen often found in Nitrox. It also stands up well in such increased oxygen conditions. As part of the move toward green fuels, Viton-lined hoses are often employed when biodiesel fuels are used.

These copolymers are often employed as mixtures with other polymers. They are compatible with many hydrocarbons but not compatible with ketones and organic acids.

8.12 NITRILE RUBBER

The copolymer of acrylonitrile and butadiene is referred to by a number of names including nitrile rubber, Buna-N, and nitrile butadiene rubber (NBR). The composition of the copolymer varies depending on what the intended end product is. Since butadiene is employed, the resulting copolymer has sites of unsaturation that are often subsequently reacted forming thermosets. The greater the amount of cross-linking, the more rigid the product along with the corresponding decreased porosity and diffusion properties. The greater the proportion of acrylonitrile incorporated into the copolymer, the greater the resistance to oils, fuels, and other chemicals and the stiffer the material. Also, the form of the butadiene monomer can vary.

Typically, NBR has a wide operational temperature range of about -40°C to 120°C making it useful for extreme automotive applications as well as cooling units. Its good resistance to oils and other chemicals allows its use around ketones, hydrocarbon liquids, esters, and aldehydes. In the lab, many of the gloves are nitrile. These gloves are also used in home and industrial cleaning and medically as examination and disposable gloves. Nitrile gloves have greater puncture resistance compared to rubber gloves. NBR's ability to withstand extreme temperatures and resistance to oils encourages their automotive uses as hoses, seals, belts, oil seals, and grommets. NBR is also used as adhesives, expanded foams, floor mats, and surface treatment of paper, synthetic leather, and footwear.

NBR is often synthesized using a radical initiating agent. Thus, emulsifier, acrylonitrile, butadiene, catalysts, and radical initiators are added to the reaction vessel. The vessel is heated to 30°C – 40°C for the formation of the so-called hot NBR aiding in the polymerization process and promoting branch formation. Reaction continues for about 5–12 hours to about 70% conversions when a terminating agent such as dimethyldithiocarbamate or diethylhydroxylamine is added. The production of cold NBR is similar except that the polymerization temperature is in the range of 5°C – 15°C . Lower temperature NBR contains less branching generally producing a somewhat stiffer product. Unreacted monomer is removed and reused in a subsequent reaction. The latex is filtered, removing unwanted solids, and then sent to blending tanks where an antioxidant is added. The resulting latex is coagulated by addition of aluminum sulfate, calcium chloride, or other coagulating compound. The latex is dried giving a flaky crumb like product that is then used to produce the desired product. Because of the variation in reactants and conditions of polymerization, there exists a variation in product structure.

8.12.1 LABORATORY GLOVES

One of the major items for laboratory safety involves the appropriate choice of gloves. Just as there is a wide variety of conditions, there is a variety of gloves; each of them involves polymeric materials. Table 8.4 is a listing of some of these gloves, some of which are shown in Picture 8.3. It must be remembered that thickness is also a consideration in the protection given by a glove with increased thickness giving increased protection but less flexibility.

TABLE 8.4 Gloves Used to Protect against Various Chemical Agents

Glove Material	Typical Uses/Properties
Asbestos	Resistant to heat
Butyl	Offers good protection toward most gases and water vapor; good for use with esters and ketones; poor for use with alcohols and phenols, halogenated and aromatic solvents
Natural (latex) rubber	Generally thin offering protection against very dilute acids and bases; poor protection toward organics
Neoprene	Good protection against acids, bases, fuels, hydrocarbons, alcohols, phenols, and peroxides; poor protection against halogenated and aromatic hydrocarbons
Nitrile	Good general-purpose glove; thicker gloves offer good protection against cuts, puncture, and abrasion
Poly(vinyl chloride)	Good resistance against abrasion and protection against acids and fats; poor protection toward most organics
Poly(vinyl alcohol)	Good impermeability to gases and aromatic and chlorinated solvents; not for use for aqueous solutions
Viton™	Most chemical resistant of synthetic rubber gloves; offers protection against many toxic and permeating chemicals including many chlorinated chemicals and aromatic liquids



PICTURE 8.3 Gloves are a mandatory safety item for chemists. They are constructed of many different materials for use with different conditions. Pictured here are a variety of gloves.

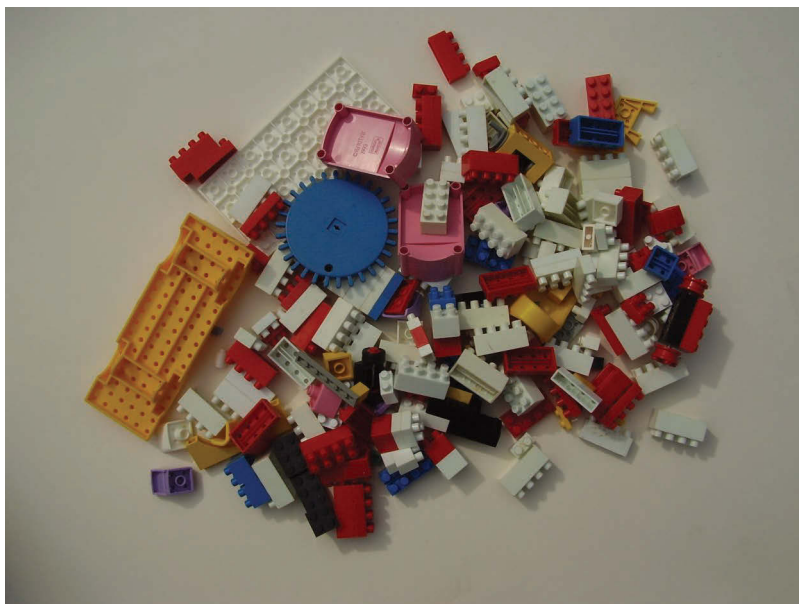
8.13 ACRYLONITRILE BUTADIENE STYRENE TERPOLYMERS

The terpolymer formed from reaction of acrylonitrile, butadiene, and styrene is referred to by the first letters of the three monomers, ABS. It is made by polymerizing acrylonitrile and styrene in the presence of polybutadiene. The proportions of reactants vary widely but are generally in the range of 15%–35% acrylonitrile, 5%–30% butadiene, and 40%–60% styrene. The resulting product contains long butadiene chains captured by shorter chains of poly(acrylonitrile-*co*-styrene). The polar nitrile groups attract one another binding the mixture together resulting in a material that is stronger than simply PS. The “plastic” styrene contributes a shiny product with surface that is largely impervious. The “rubbery” polybutadiene contributes resilience and a wide range of operating temperatures between -25°C and 60°C . This combination results in what is referred to as “[rubber toughening](#)” where the rubbery polybutadiene is dispersed within a plastic or more rigid styrene matrix bound together by the acrylonitrile units. Typically, impacts are transferred from the more rigid styrene-rich portions to the rubbery butadiene-rich regions that are able to help absorb the impact through segmental chain movement. Impact resistance can be increased by increasing the amount of polybutadiene up to a limit. Aging is also dependent on the ABS composition and is generally dependent on the amount of butadiene since the unsaturation is typically responsible for limiting the use time because of the increased cross-linking, consequently increased brittleness, with time. Thus, it is customary to add an antioxidant to curtail aging.

The properties of the end product are dependent on the processing conditions. For instance, processing the ABS at higher temperatures increases the gloss and heat resistance of the material, while increased impact resistance and strength result lower processing temperatures.

The electrical properties of ABS are relatively independent over a wide range of applied frequencies making it a good material where varied electrical frequencies are present.

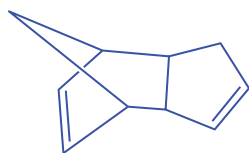
ABS is used to make rigid molded products such as piping and fittings, fuel tanks, automotive body parts, toys, wheel covers, and enclosures and where good shock absorbance is needed such as golf club heads and protective head gear. In fact, our ever-present Lego building blocks are made from ABS plastic (Picture 8.4).



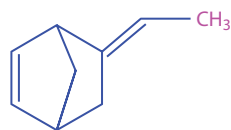
PICTURE 8.4 ABS children's building blocks.

8.14 EPDM RUBBER

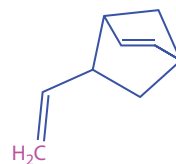
EPDM rubber's name is derived from E for ethylene, P from propylene, D from diene, and M from the ASTM rubber classification. The dienes currently employed are dicyclopentadiene (8.30), ethylidene norbornene (8.31), and vinyl norbornene (8.32). Along with supplying the needed double bond for subsequent cross-linking (curing), the dienes also supply steric hindrance encouraging amorphous formation.



Dicyclopentadiene (8.30)



Ethylidene norbornene (8.31)



5-Vinyl-2-norbornene (8.32)

The ethylene content is about 45%–75%, and diene content is about 2.5%–12%, with the remainder being propylene. The greater the ethylene content, the higher the loading capability and better mixing and extrusion of the material. The polymers are cured employing a peroxide agent.

EPDM rubbers have excellent ozone, weather, and heat properties. While it is compatible with fireproofing hydraulic fluids, water, and bases, it is not compatible with most gasoline and other hydrocarbon liquids, concentrated acids, and halogen-intense solvents. The automotive industry uses EPDM rubbers as weather seals including door, trunk, hood, and window seals. The noise in automobiles may be the result of the friction between the EPDM seals and the mated surface. This is normally corrected for by using a special coating that also increases the chemical resistance of the rubber. EPDM is also used to waterproof roofs. As a green material application, it allows the harvesting of rainwater for other uses since it does not introduce pollutants into the rainwater.

EPDM rubber is also used to produce garden hoses, washers, belts, tubing, electrical insulation, mechanical goods, motor oil additive, pond liner, and RV roofs and as an impact modifier.

SUMMARY

1. Unlike homopolymers, which consist of chains with identical repeating units, copolymers are macromolecules that contain two or more unlike units. These repeat units may be randomly arranged or may alternate in the chain. Block copolymers are linear polymers that consist of long sequences of repeating units in the chain, and graft copolymers are branch polymers in which the branches consist of sequences of repeating units that differ from those present in the backbone. These different copolymers give materials with differing properties, even when synthesized using the same monomers.
2. The copolymerization between two different monomers can be described using only four reactions, two homopolymerizations and two cross-polymerization additions. Through appropriate arrangements, equations that allow copolymer composition to be determined from the monomer feed ratio are developed.
3. The product of the reactivity ratios can be used to estimate the copolymer structure. When the product of the reactivity ratios is near one, the copolymer arrangement is random; when the product is near zero, the arrangement is alternating; when one of the reactivity ratios is large, blocks corresponding to that monomer addition will occur.
4. Block and graft copolymers may differ from mixtures by having properties derived from each component. Block copolymers can be used as thermoplastic elastomers and graft copolymers with flexible backbones can be used for high-impact plastics. Block and graft copolymers can be produced by step and chain reaction polymerization. The principal block copolymers are thermoplastic elastomers and elastic fibers such as ABS. Principal graft copolymers are grafted starch and cellulose.
5. Blends are physical mixtures of polymers. Depending on the extent and type of blend, the properties may be characteristic of each blend member or may be some "blend" of properties. Immiscible blends are phase separated with the phases sometimes chemically connected. They are generally composed of a continuous and discontinuous phase. HIPS is an example of an immiscible blend. Miscible blends occur when the two blended materials are compatible. Often the properties are a mixture of the two blended materials. The plastic automotive panels and bumpers are generally made from a miscible blend of polyethylene and a copolymer of polyethylene and polypropylene.
6. Dendrites are complex molecules formed from building up of the dendrite by individual steps (divergent growth) or from bringing together the units already formed (convergent growth).
7. Ionomers are often referred to as processable thermosets. They are cross-linked through the use of metal ions such that application of heat and pressure allows them to be reformed.

GLOSSARY

AB: Block copolymer with two separate mers.

ABA: Block copolymer with three sequences of mers in the order shown.

ABS: Three-component copolymer of acrylonitrile, butadiene, and styrene.

Alloy: Rubber-toughened materials in which the matrix can be a mixture of polymer types.

Alternation copolymer: Ordered copolymer in which every other building is a different mer.

Azeotropic copolymer: Copolymer in which the feed and composition of the copolymer are the same.

Blends: Mixtures of different polymers on a molecular level; may exist in one or two phases.

Block copolymer: Copolymer that contains long sequences or runs of one mer or both mers.

Buna-N: Elastomeric copolymer of butadiene and acrylonitrile.

Buna-S: Elastomeric copolymer of butadiene and styrene.

Butyl rubber: Elastomeric copolymer of isobutylene and isoprene.

Charge-transfer complex: Complex consisting of an electron donor (D) and an electron acceptor (A) in which an electron has been transferred from D to A resulting in the charge-transfer agent $D^+ A^-$.

Composites: Mixtures of different polymers, one forming a continuous phase (the matrix) and one the discontinuous phase (often a fiber).

Compositional drift: Change in composition of a copolymer that occurs as copolymerization takes place with monomers of different reactivities.

Copolymer: Macromolecule containing more than one type of mer in the backbone.

Dendrites: Complex molecules that are highly branched.

Domains: Sequences in a block copolymer or polymer.

Graft copolymer: Branched copolymer in which the backbone and the branches consist of different mers.

Homopolymer: Macromolecule consisting of only one type of mer.

Hytrell: Trade name for a commercial TEP.

Ideal copolymer: Random copolymer.

Interpenetrating polymer network (IPN): Intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and/or cross-linked in the immediate presence of the other.

Ionomers: Copolymers typically containing mostly ethylene units, with the remaining units being ion containing that are neutralized through reaction with metals.

Kraton: Trade name for an ABA block copolymer of styrene and butadiene.

Living polymers: Macrocarbanions.

Polyallomers: Block copolymers of ethylene and propylene.

Q–e scheme: A semiempirical method for predicting reactivity ratios.

Random copolymer: Copolymer in which there is no definite order for the sequence of the different mers.

Reactivity ratio: Relative reactivity of one monomer compared to another monomer.

Saran: Trade name for copolymer of vinyl chloride and vinylidene chloride.

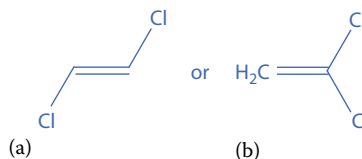
SBR: Elastomer copolymer of styrene and butadiene.

Spandex: Elastic fiber consisting of a block copolymer of a polyurethane, hard segment, and a polyester or polyether, soft segment.

Wall equation: Predecessor to the copolymer equation.

EXERCISES

1. Draw representative structures for (a) homopolymers, (b) alternation copolymers, (c) random copolymers, (d) AB block copolymers, and (e) graft copolymers of styrene and acrylonitrile.
2. If equimolar quantities of M_1 and M_2 are used in an azeotropic copolymerization, what is the composition of the feed after 50% of the copolymer has formed?
3. Define r_1 and r_2 in terms of rate constants.
4. Do the r_1 and r_2 values increase or decrease during copolymerization?
5. What is the effect of temperature on r_1 and r_2 ?
6. What will be the composition of copolymers produced in the first part of the polymerization of equimolar quantities of vinylidene chloride and vinyl chloride?
7. What monomer may be polymerized by anionic, cationic, and free radical chain techniques?
8. Which chain polymerization technique would you select to polymerize (a) isobutylene, (b) acrylonitrile, and (c) propylene?
9. If $r_1 r_2$ is about zero, what type of copolymer would be formed?
10. Show a structure for an AB block copolymer.
11. What is the value of $r_1 r_2$ for an ideal random copolymer?
12. Which would polymerize more readily?



13. Why are most elastomers difficult to recycle?
14. What is the composition of the first copolymer chains produced by the copolymerization of equimolar quantities of styrene and methyl methacrylate in (a) free radical, (b) cationic, and (c) anionic copolymerization?
15. What is the composition of the first copolymer butyl rubber chains produced from equimolar quantities of the two monomers?
16. What is the composition of the first copolymer butyl rubber chains produced from a feed containing 9 mol of isobutylene and 1 mol of isoprene?
17. How would you ensure that production of butyl rubber of uniform composition occurs in Question 16.
18. For a graft copolymer with a backbone derived from monomer A and the graft B what often occurs when B is long?
19. What is the composition of the first polymer chains produced by the copolymerization of equimolar quantities of vinyl chloride and vinyl acetate?
20. What are the advantages, if any, of the vinyl chloride-vinyl acetate copolymer over PVC itself?
21. Why are ionomers superior to LDPE?
22. What is the difference between Buna-S, GRS, and SBR?
23. How can you connect two different phases in polymer blends?
24. Which sequence in the ABA block copolymer of ethylene oxide and propylene oxide is more lyophilic?
25. When will a blend exhibit two distinct properties.
26. Are dendrites really polymeric?
27. What product is obtained if 1.5 mol of styrene is copolymerized with 1 mol of maleic anhydride in benzene?
28. Why are ionomers referred to as processable thermosets?
29. Of what use is the copolymerization equation?
30. How could you use graft copolymerization techniques to reduce the water solubility of starch?
31. What is the end group when azobiscyanopentanoic acid is used as an initiator?

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Organometallic and Metalloid Polymers

9.1 INTRODUCTION

Classical polymer chemistry emphasizes materials derived from about a dozen elements (including C, H, O, N, S, P, Cl, and F). The following two chapters, Chapters 9 and 10, deal with polymers containing additional elements. The present chapter focuses on inorganic and metal-containing polymers containing organic units.

Elements such as silicon, sulfur, and phosphorus catenate similar to the way carbon does, but such catenation generally does not lead to (homo) chains with high degrees of polymerization. Further, such products might be expected to offer lower thermal stabilities and possibly lower bond strengths compared to carbon-based polymers since their bond energies are generally lower (Table 9.1). The alternative of using heteroatomated backbones is attractive since the resultant products can exhibit greater bond energies (Table 9.1).

One common misconception concerns the type of bonding that can occur between inorganic and organic atoms. With the exception of the clearly ionic bonding, many of the inorganic–organic bonding is of the same general nature as that present in organic compounds. The percentage contribution of the organic–inorganic bonding due to covalent contributions is typically well within that found in organic acids, alcohols, and thiol and nitro moieties (for instance, the usual limits are about 5% ionic character for the B–C bond to 55% ionic for the Sn–O and both are clearly directional bonding in character). Thus, the same spatial, geometrical rules apply to these polymers as to the more classical polymers such as PE, PS, nylons, polyesters, and PP. The exception is the ionomers where the metals are bonded through ionic bonding to the oxygen atoms.

The number of potential inorganic–organic polymers is great. The inorganic portions can exist as oxides and salts, in different oxidation states, different geometries, etc. The importance of these inorganic–organic polymers can be appreciated by considering the following. First, photosynthesis, the conversion of carbon dioxide and water by sunlight to sugars is based on a metal-containing polymer—chlorophyll. Also, a number of critical enzymes, such as hemoglobin, contain a metal site as the key site for activity. Second, the inorganic–organic polymers produced thus far exhibit a wide range of properties not common to most organic polymers, including electrical conductivity, specific catalytic operations, wide operating temperatures, greater strengths, and greater thermal stabilities (Table 9.2). Third, inorganic–organic polymers form the basis for many insulators and building materials. Fourth, inorganic elements are present in high abundances in Earth's crust (Table 9.3).

The topic of metal- and metalloid-containing polymers can be divided by many means. Here, the topic will be divided according to the type of reaction employed to incorporate the inorganic atom into the polymer chain. While many other types of reactions have been employed to produce metal- and metalloid-containing polymers including redox, coupling, and ring-opening polymerizations, the present chapter will focus on addition, condensation, and coordination reactions. Emphasis is given to unifying factors.

TABLE 9.1 General Magnitude of Bonds

Bond	General Bond		Bond	General Bond	
	Energy (kJ/mol)	Ionic Character ^a (%)		Energy (kJ/mol)	Ionic Character ^a (%)
Al–O	560	60	P–O	400	40
B–C	360	5	P–S	320	5
B–N	440	20	S–S	240	0
B–O	460	45	Si–Si	220	0
Be–O	500	65	Si–C	300	10
C–C	340	0	Si–N	420	30
C–H	400	5	Si–O	440	50
C–N	300	5	Si–S	240	10
C–O	340	20	Sn–Sn	160	0
C–S	260	5	Sn–O	520	55
P–P	200	0	Ti–O	640	60
P–N	560	20			

^a Based on Pauling electronegativity values. The percentage of ionic bonding should be less where pi bonding occurs. Given to nearest 5%.

TABLE 9.2 Actual and Potential Applications for Organometallic and Metalloid Polymers

Biological	Anticancer, antiviral, treatment of arthritis, antibacterial, antifungal, antifouling, treatment of Cooley's anemia, algicides, molluscicides, contrast agents, radiology agents
Electrical/optical	Nonlinear optics, lithography, conductors, semiconductors, piezoelectric, pyroelectric, solar energy conversion, electrodes, computer chip circuitry
Analytical, catalytic, building	UV absorption, smart materials, nanocomposites, laser, sealants, paints, caulks, lubricants, gaskets

TABLE 9.3 Relative Abundances of Selected Elements in Earth's Upper (10 Miles) Crust

Element	Weight (%)	Element	Weight (%)
Oxygen	50	Titanium	0.4
Silicon	26	Fluorine	0.3
Aluminum	7.3	Chlorine	0.2
Iron	4.2	Carbon	0.2
Calcium	3.2	Sulfur	0.1
Sodium	2.4	Phosphorus	0.1
Potassium	2.3	Barium	0.1
Magnesium	2.1	Manganese	0.1
Hydrogen	0.4		

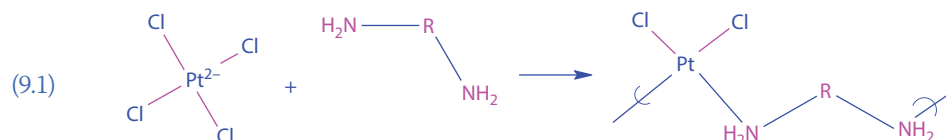
9.2 INORGANIC REACTION MECHANISMS

Many of the polymerizations and monomer syntheses are simply extensions of known inorganic, organometallic, and organic reactions. The types and language used to describe inorganic–organic reaction mechanisms are more diversified than those employed by classical organic chemists.

The majority of inorganic reactions can be placed into one of the two broad classes—oxidation–reduction (redox) reactions including atom and electron transfer reactions and substitution reactions. Terms such as inner sphere, outer sphere, and photo-related reactions are employed to

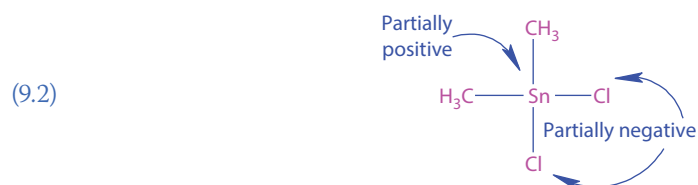
describe redox reactions. Such reactions are important in the synthesis of polymers and monomers and in the use of metal-containing polymers as catalysts and in applications involving transfer of heat, electricity, and light. They will not be dealt with to any appreciable extent in this chapter.

Terms such as lability, inertness, ligand, associative, interchange, and dissociative are important when discussing substitution reactions. The ligand is simply (typically) the Lewis base that is substituted for and is also the agent of substitution. Thus, in the reaction between tetrachloroplatinate and diamines forming the anticancer and antiviral platinum II polyamines, the chloride is the leaving group or departing ligand, while the amine-functional group is the ligand that is the agent of substitution.



There is a difference between the thermodynamic terms stable and unstable and the kinetic terms labile and inert. Furthermore, the difference between the terms stable and unstable and the terms labile and inert is relative. Thus, $\text{Ni}(\text{CN})_4^{-2}$ and $\text{Cr}(\text{CN})_6^{-3}$ are both thermodynamically stable in aqueous solution, yet kinetically, the rate of exchange of radiocarbon-labeled cyanide is quite different. The half-life for exchange is about 30 seconds for the nickel complex and 1 month for the chromium complex. Taube has suggested that those complexes that react completely within about 60 seconds at 25°C be considered labile while those that take a longer time be called inert. This rule of thumb is often given in texts but is not in general use in the literature. Actual rates and conditions are superior tools for the evaluation of the kinetic/thermodynamic stability of complexes.

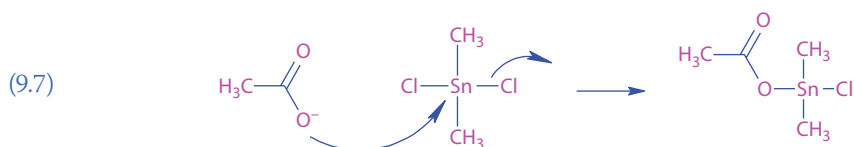
Many polymer-forming reactions that occur at metal-atom sites can be considered as Lewis acid-base reactions. Thus, for reactions involving an organotin dichloride, the electronegativities of the chlorides are greater than that of the tin causing the tin to be somewhat electron deficient or partially positive. Thus, the tin atom can be considered a Lewis acid and is electropositive and a possible site for “attack” by a Lewis base or nucleophile (9.2).



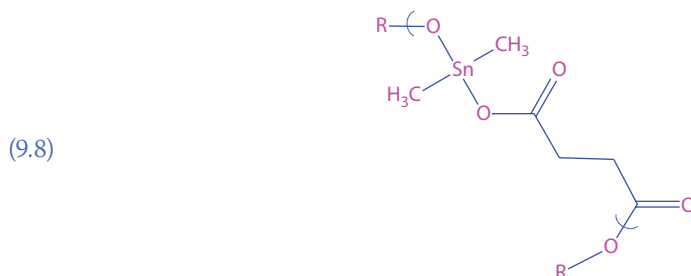
The non-metal-containing molecule contains a heteroatom that has electrons that can be donated, that is, it is a nucleophile or Lewis base, 9.3 through 9.6.



The Lewis acid and base reacts forming a covalent bond. For the reaction between the salt of an acid and a tin dihalide, this can be described as shown in the following equation:



For a diacid, this can result in the formation of a polymer (9.8).



In naming the type of polymer, the tin moiety is treated as a methylene group so this linkage is called an ester and the resulting polymer is called a polyester. The reaction between a diamine and dihalotin forms an amine, $\text{Sn}-\text{NH}-\text{R}$, linkage so the polymer is called a polyamine or organotin polyamine. The reaction between a diol or dialcohol forms ether linkages, $\text{Sn}-\text{O}-\text{R}$, so the polymer is called a polyether or organotin polyether.

The reaction between the Lewis acid and Lewis base is commonly referred to as a bimolecular nucleophilic substitution reaction or $\text{S}_{\text{N}}2$ reaction. In truth, with organometallic reactions, the precise reaction is often more difficult to describe because of the presence of available “d” orbitals on the organometallic atom, here tin.

The following is a brief description of typical interchange mechanisms at organometallic metal-atoms.

The term “D mechanism” (dissociation) is loosely comparable to $\text{S}_{\text{N}}1$ -type reaction mechanisms, but it does not imply an observed rate law. Here, a transient intermediate is assumed to live long enough to be able to differentiate between various ligands, including the one just lost, and between solvent molecules. Thus, the overall rate expression may be dependent on the nature of LL' , solvents, or some combination as pictured in the following equations where S is the solvent, L is the leaving ligand, and L' is the incoming ligand:



In the I_{d} mechanism, dissociative interchange, the transition state involves extensive elongation of the $\text{M}\cdots\text{L}$ bond but not rupture:



The $\text{ML}_3\text{L}'$ species is often called an outer sphere complex, or if ML_4 is a cation and L, an anion, the couple is called an ion pair.

For the I_{a} mechanism, associative interchange, the interaction between M and L' is more advanced in the transition state than in the case of the I_{d} . The $\text{M}\cdots\text{L}'$ bonding is important in defining the activated complex. Both of these interchange mechanisms are loosely connected to the $\text{S}_{\text{N}}2$ -type mechanism.

For the A mechanism, associative, there is a fully formed intermediate complex ML_4L' , which then dissociates, being roughly analogous to the E_1 type reaction mechanism.

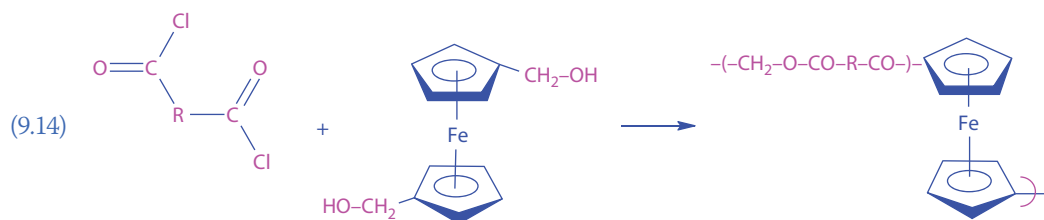
It is important to remember that the same electronic, steric, mechanistic, kinetic, and thermodynamic factors that operate in regard to smaller molecules are in operation during a polymerization process.

9.3 CONDENSATION ORGANOMETALLIC POLYMERS

Condensation reactions exhibit several characteristics such as (typically) expulsion of a smaller molecule on reaction leading to a repeat unit containing fewer atoms than the sum of the two reactants, and most reactions can be considered in terms of polar (Lewis acid–base; nucleophilic–electrophilic) mechanisms. The reaction site can be at the metal atom (i.e., adjacent to the atom)



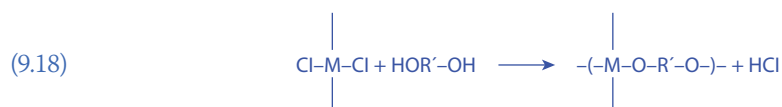
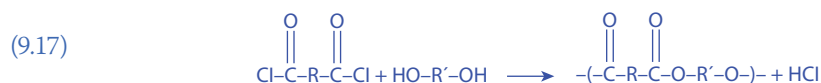
or it can be somewhat removed from the metal site.



Research involving condensation organometallic polymers was catalyzed by the observation that many organometallic halides possess a high degree of covalent character within their composite structure and that they can behave as organic acid chlorides in many reactions, such as hydrolysis



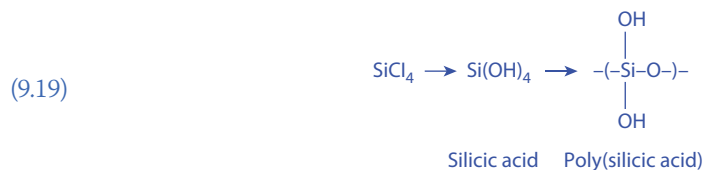
and polyesterification.



Thus, many of the metal-containing polycondensations can be considered as extensions of organic formation of polyesters, polyamides, etc., reactions.

The most important organometalloid polymers are the polysiloxanes based on the siloxane Si–O linkage found in glass and quartz (Chapter 10). The polysiloxanes were incorrectly named silicones by Kipping in the 1920s, but this name continues to be widely used. Originally, it was wrongly believed to have a structure similar to a ketone, hence, silicone.

The production of silicate glass is believed to be a transcondensation of the siloxane linkages in silica. A comparable poly(silicic acid) is produced when silicon tetrachloride is hydrolyzed.



The poly(silicic acid) further condenses producing a cross-linked gel. This cross-linking can be prevented by replacing the hydroxyl groups in silicic acid with alkyl groups. Ladenburg prepared the first silicone polymer in the nineteenth century by the hydrolysis of diethyldiethoxysilane. Kipping, in the early 1940s, recognized that these siloxanes could also be produced by the hydrolysis of dialkyldichlorosilanes giving a poly(silicic acid)-like structure where the hydroxyl groups are replaced by alkyl groups.

In 1945, Rochow discovered that a silicon-copper alloy reacted with organic chlorides forming a new class of compounds called organosilanes.

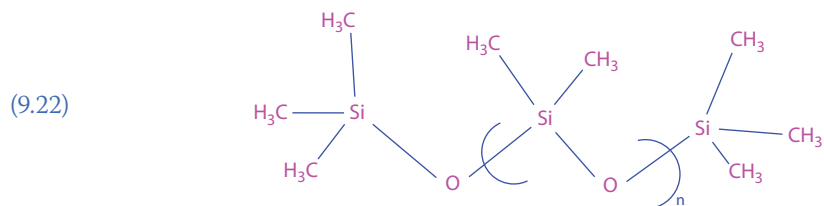


These compounds react with water-forming dihydroxysilanes:

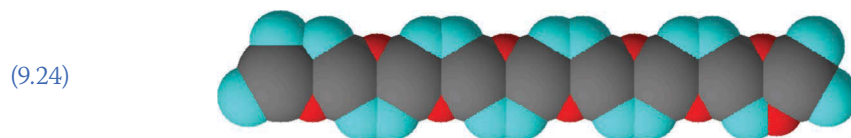
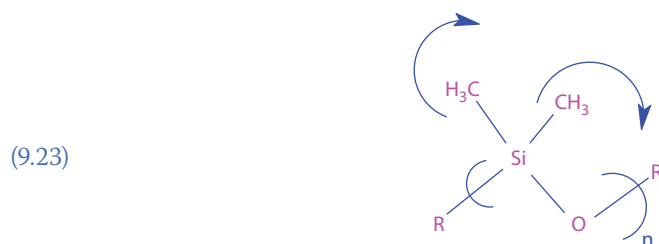


and eventually dimeric, oligomeric, and finally polysiloxanes (9.21). Because of the toxicity of HCl, the chlorine groups are replaced by acetate groups leading to the familiar vinegar smell for many silicon caulks and sealants. Branching and cross-linking were introduced through the use of [methyltrichlorosilane](#). Modern caulks and sealants are made using the tetrafunctional group tetraethoxysilane to introduce cross-linking into the resin.

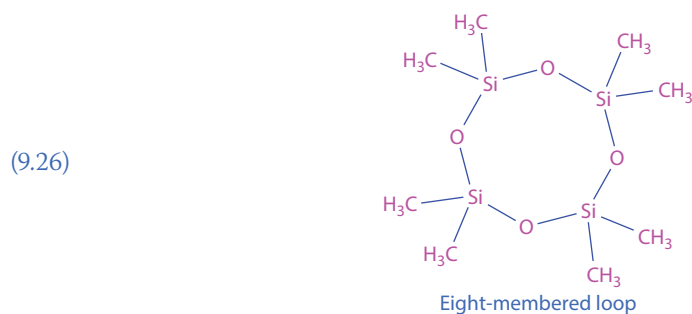
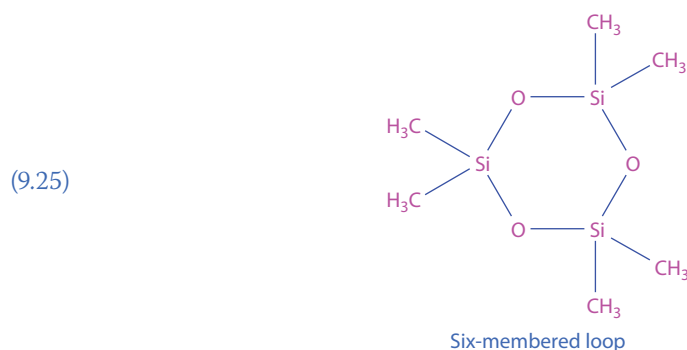
Polysiloxanes are characterized by combinations of chemical, mechanical, and electrical properties that taken together are not common to any other commercially available class of polymers. They exhibit relatively high thermal and oxidative stability, low power loss, high dielectric strength, and unique rheological properties and are relatively inert to most ionic reagents. Almost all of the commercially utilized siloxanes are based on polydimethylsiloxane with trimethylsiloxy end groups. They have the widest-use temperature range for commercial polymers suitable for outdoor applications from the winter of Nome, Alaska, to the summer of South Florida (about -60°C to 40°C). The first footprints on the moon were made with polysiloxane elastomeric boots.



The reason for the low-temperature flexibility is because of a very low T_g , about -120°C , which is the result of the methyl groups attached to the silicon atoms being free to rotate causing the oxygen and other surrounding atoms to “stay away” creating a flexible chain (9.23). This is further illustrated with the space-filling model of a portion of a dimethylsiloxane chain shown in Equation 9.24 where the methyl groups shown in light blue are crowded by methyl groups on adjacent silicon atoms. The crowding forces the somewhat elongated O–Si–O arrangements, not shown in the model, discouraging formation of pi overlap between the Si and O atoms and allowing the rotation of the methyl groups.



Polysiloxanes degrade by an unzipping mechanism forming six- and eight-membered rings. They also form these same rings when polymerized forming what is referred to as “wasted loops” because they must be removed before the polysiloxane is useful. This tendency to form six- and eight-membered rings is based on the good stability of such siloxane rings.



Polysiloxanes are used in a wide variety of applications. The viscosity or resistance to flow increases as the number of repeat units increases but physical properties such as surface tension and density remain about the same after a DP of about 25. The liquid surface tension is lower than the critical surface tension of wetting resulting in the polymer spreading over its own absorbed films. The forces of attraction between polysiloxane films are low resulting in the formation of porous films that allow oxygen and nitrogen to readily pass through but not water. Thus, semi-permeable membranes, films, have been developed that allow divers to “breathe air under water” for short periods.

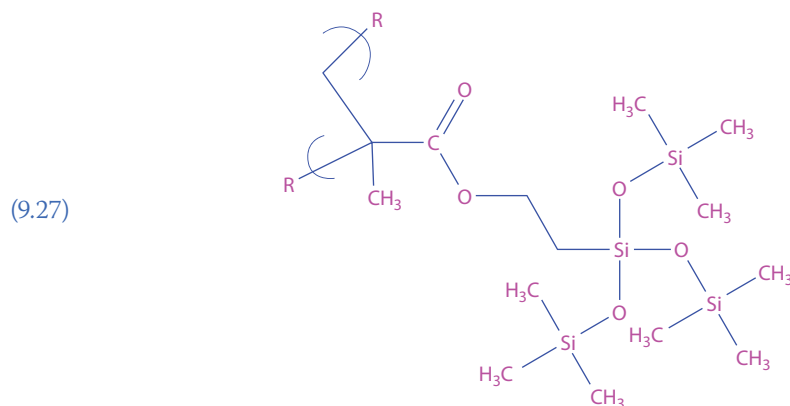
As noted earlier, viscosity increases with DP allowing many of the uses to be grouped according to chain length. Low-viscosity fluids with DPs of 2–30 are used as antifoams and in the flow control of coatings applications. These applications are the direct consequence of the low attractions between polysiloxane chains that, in turn, is responsible for their low surface tension. Thus, they encourage a coatings material to flow across the surface filling voids, corners, and crevices. Their good thermal conductivity and fluidity at low temperatures allow their use as low-temperature heat exchangers and in low-temperature baths and thermostats.

Viscous fluids correspond to a DP range of about 50–400. These materials are employed as mold release agents for glass, plastic, and rubber parts. They are good lubricants for most metal to nonmetal contacts. They are used as dielectric fluids (liquids) in a variety of electrical applications including transformers and capacitors, as hydraulic fluids in vacuum and hydraulic pumps, in delicate timing and photographic devices, as antifoam agents, as components in protective hand creams, as toners in photocopiers, in oil formulations when mixed with thickeners, and in inertial guidance systems. High-performance greases are formed by mixing the polysiloxane fluids with polytetrafluoroethylene or molybdenum disulfide. Brake fluids are formulated from polydimethylsiloxane fluids with DPs about 50. High-viscosity fluids with DPs about 700–6000 are used as damping fluids for weighting meters at truck stops. They act as liquid springs in shock absorbers. The longer chained fluids are used as impact modifiers for thermoplastic resins and as stationary phases in gas chromatography.

As with the alkanes, even longer chains form the basis for solid polysiloxanes that, according to design, can be classified as thermoplastics, engineering thermoplastics, elastomers, and when cross-linked, as thermosets. Solid polysiloxanes are used in a variety of applications including as sealants, thermostripping, caulking (Picture 9.1), dampening, O-rings, and window gaskets. Weather stripping on cooling units, trucks, and automobiles is often made of polysiloxanes.

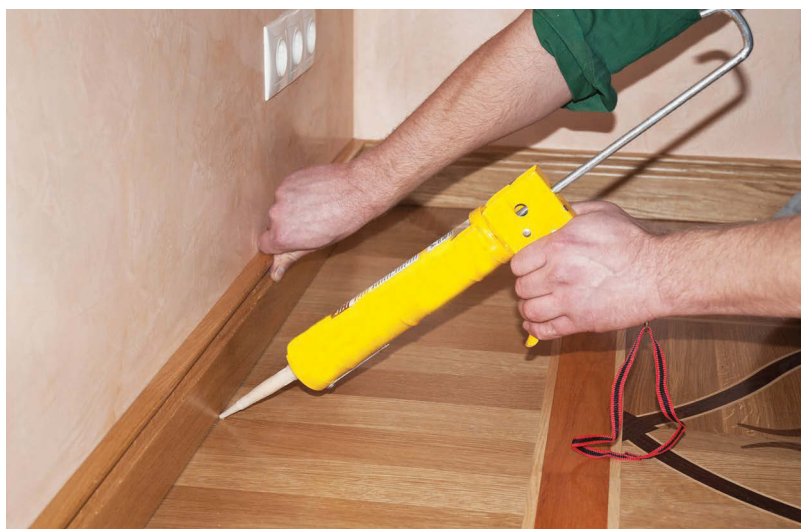
Room-temperature-vulcanizing silicon rubbers make use of the room temperature reaction of certain groups that can be placed on polydimethylsiloxanes that react with water. When exposed to water, such as that normally present in the atmosphere, cross-links are formed creating an elastomeric product.

The first contact lenses were based on poly(methyl methacrylate). While they could be polished and machined, they did not permit gas exchange and were rigid. By the early 1970s, these were replaced by soft contact lenses containing cross-linked poly(2-hydroxyethyl methacrylate). These so-called disposable lenses do permit gas exchange. More recently, Salamone and coworkers developed contact lenses based on the presence of siloxane units. Polysiloxanes have good gas permeability. These polymers are referred to as Tris materials and are generally copolymers containing units as shown in the following:



Polysiloxanes are widely employed as biomaterials. Artificial skin can be fabricated from a bilayer fabricated from a cross-linked mixture of bovine hide, collagen, and chondroitin sulfate derived from shark cartilage with a thin top layer of polysiloxane. The polysiloxane acts as a moisture and oxygen-permeable support and to protect the lower layer from the “outer world.” A number of drug delivery systems use polysiloxanes because of the flexibility and porous nature of the material.

The first Silly Putty (TM), also called Nutty Putty, was made over 50 years ago from mixing together silicone oil with boric acid. That original formula has changed only a little though colorants have been added giving the material brighter colors and some the ability to “glow in the dark.” Today, the formula contains about 70% dimethylsiloxane and boric acid, 17% quartz, 9% Thixatrol ST (a commercial rheology modifier, i.e., a derivative of castor oil), and several other minor constituents. Silly Putty is a dilatant material (Section 13.1) meaning it has an inverse thixotropy (a thixotropic liquid is one whose viscosity decreases with time). In essence, the resistance



PICTURE 9.1 Application of silicone caulk. (From Shutterstock, <http://www.shutterstock.com/pic.mhtml?id=333272852&src=id>.)

of flow increases faster than the rate of flow. Thus, under short interaction times (Section 13.1), it behaves as a solid where the various molecular components resist ready movement acting as a solid, and under sharp impact like hitting it with a hammer or rapidly “snapping” it, it will act as a brittle material. Under a relatively long interaction time, the molecular chains are able to yield and the material acts as a liquid. Under moderate interaction times, there is segmental movement and the material acts as a rubber.

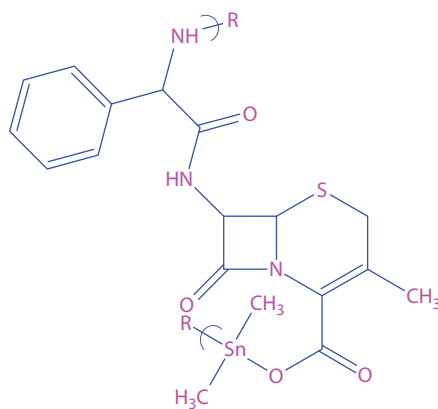
Silly Putty is one of the several materials whose discovery occurred at about the same time by different individuals. In this case, the two individuals are Earl Warrick, working for Dow Corning, and James Wright, a researcher for General Electric. The discoveries occurred in 1943 during searches for synthetic rubber during World War II. Initially, no practical use was found. By 1949, it was found in a local toy store as a novelty item. Despite its good sales, the store dropped it after 1 year. The next year, Peter Hodson began packaging it in the now familiar plastic egg. Today, it sells for about the same price it did in 1950. Silly Putty sells at a rate of about 6 million eggs, or 90 tons, yearly.

Carraher and coworkers have produced a wide variety of organometallic condensation polymers based on the Lewis acid–base concept. Polymers have been produced from Lewis bases containing amine, alcohol, acid, thiol, and related units including a number of drugs such as ciprofloxacin and acyclovir. The Lewis acids contain such metals and metalloids as Ti, Zr, Hf, V, Nb, Si, Ge, Sn, Pb, As, Cu, Ni, Sb, Bi, Mn, Ru, P, Co, and Fe. These compounds have potential uses in the biomedical arena as antifungal, antibacterial, anticancer, Parkinson’s treatment, and antiviral drugs. These polymers show promise in a wide variety of other areas including electrical, catalytic, and solar energy conversion. Polymers referred to as polydyes, because of the presence of dye moieties in the polymer backbones, have impregnated paper products, plastics, rubber, fibers, coatings, and caulks giving the impregnated material color, (often) added biological resistance, and special photo properties.

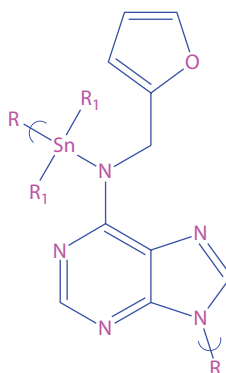
Organotin compounds are the most widely used metal-containing compounds. The bulk of these materials are employed to improve the heat stability of PVC as it is formed into piping. Today, because polymers leach much slower than small molecules, organotin polymers initially synthesized by Carraher and coworkers are being used in PVC piping. Organotin polyamine containing the plant growth hormone kinetin (9.28) increases the germination of damaged seeds and thus may help in providing food in the third-world countries. It also increases the germination rate of saw grass seed from about 0% to over 50% and is an important agent in replacing the “sea of grass” (actually saw grass) in the Everglades. Some of the organotin polymers are found to be effective anticancer, antibacterial, and antiviral agents (one such polymer is shown (9.29)). They show good inhibition of several ovarian cancer test

lines and of a wide variety of viruses including those responsible for smallpox, herpes simplex, chickenpox, and shingles.

(9.28)



(9.29)



Some of the polymers, including the metallocene-containing products, show the ability to control laser radiation. Depending on the range of radiation, laser energy can be focused allowing the material to be cut readily, or it can be dispersed imparting to the material containing the polymer-added stability toward the radiation.

A number of these polymers exhibit a phenomenon called “anomalous fiber formation,” reminiscent of “metallic whiskers.”

9.4 COORDINATION POLYMERS

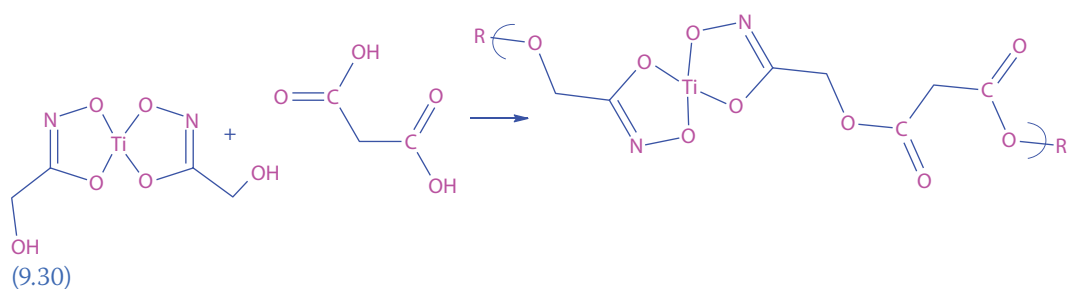
Coordination polymers have served humankind since before recorded history. The tanning of leather and generation of selected colored pigments depend on the coordination of metal ions. A number of biological agents, including plants and animals, owe their existence to coordinated polymers such as hemoglobin. Many of these coordination polymers have unknown and/or irregular structures.

The drive for the synthesis and characterization of synthetic coordination polymers was catalyzed by work supported and conducted by the U.S. Air Force in a search for materials that exhibited high thermal stabilities. Attempts to prepare highly stable, tractable coordination polymers were disappointing. Typically, only oligomeric products were formed and the monomeric versions were often more stable than the polymeric versions.

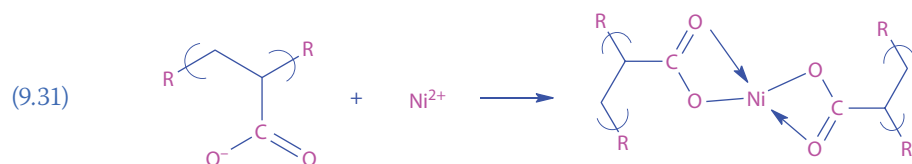
Bailar listed a number of principles that can be considered in designing coordination polymers. Briefly, these are as follows: (1) Little flexibility is imparted by the metal ion or within its immediate environment; thus, flexibility must arise from the organic moiety. Flexibility increases as the covalent nature of metal–ligand bond increases. (2) Metal ions only stabilize ligands in their immediate vicinity; thus, the chelates should be strong and close to the metal ions. (3) Thermal, oxidative, and hydrolytic stability are not directly related; polymers must be

designed specifically for the properties desired. (4) Metal–ligand bonds have sufficient ionic character to permit them to rearrange more readily than typical “organic bonds.” (5) Polymer structure (such as square planar, octahedral, linear, network) is dictated by the coordination number and stereochemistry of the metal ion or chelating agent. Finally, (6) employed solvents should not form strong complexes with the metal or chelating agent, or they will be incorporated into the polymer structure and/or prevent reaction from occurring.

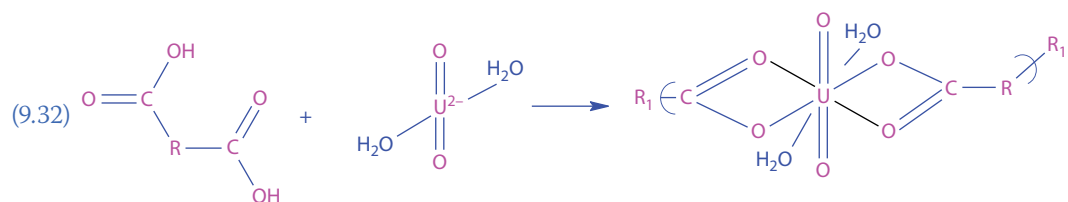
Coordination polymers can be prepared by a number of routes, with the three most common being (1) preformed coordination metal complexes polymerized through functional groups where the actual polymer-forming step may be a condensation or addition reaction



(2) reaction with polymer-containing ligands or



(3) polymer formation through chelation



Carraher and coworkers employed the last two processes to recover the uranyl ion. The uranyl ion is the natural water-soluble form of uranium oxide. It is also toxic, acting as a heavy metal toxin. Through the use of salts of dicarboxylic acids and poly(acrylic acid), the uranyl ion was removed to 10^{-5} M with the resulting product much less toxic and convertible to uranium oxide by heating.

Many of the organometallic polymers are semiconductors with bulk resistivities in the range of 10^3 – 10^{10} Ω cm suitable for specific semiconductor use. Further, some exhibit interesting photo properties.

In 1964, Rosenberg and coworkers found that bacteria failed to divide but continued to grow. After much effort, they found that the cause of this anomalous growth was a broken electrode and eventually identified the chemical as *cis*-dichlorodiamineplatinum II. This compound is now licensed under the name Platinol and is also known as cisplatin. Cisplatin is the most widely used anticancer drug. Carraher, Rosenberg, Allcock, and others have reduced the toxic effects of cisplatin through placement of the platinum moiety into various coordination platinum polymers. Some of these polymers inhibit various cancer growths with much less toxic effects. Carraher and coworkers also found that many of these are also very active antiviral agents and some are able to prevent the onset of virally related juvenile diabetes in test animals.

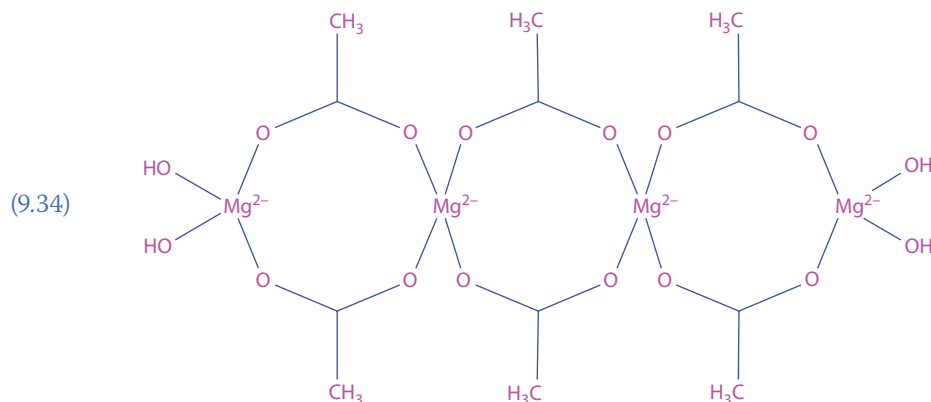
Simple chelation polymers are all about us, but they are not always recognized as such. During the winter, the north experiences freezing temperatures and the associated ice. Sodium chloride

and calcium chloride are the most used freezing point lowering agents. They are inexpensive and readily available. On the negative side, they adversely affect surrounding plant life and must be reapplied generally after each rain–ice cycle.

Recently, magnesium acetate has begun to be used for application in especially dangerous sites such as bridges. The acetate can be either internally bridged, where it is not polymeric,



or it can be bridged forming a complex linear polymeric material.



Hellmuth believes that the polymeric material forms (9.34). If the magnesium acetate were simply the internally chelated material, then it should be quickly washed away. The combination of calcium and magnesium acetates is known as CMA. CMA is more expensive than sodium chloride or calcium chloride, but it does not damage plant life and it has a much longer effective life. The polymer seeks the cracks and crevices in and around the pavement and remains until needed again to lower the freezing point of water. Often, one application of CMA is sufficient for a winter season.

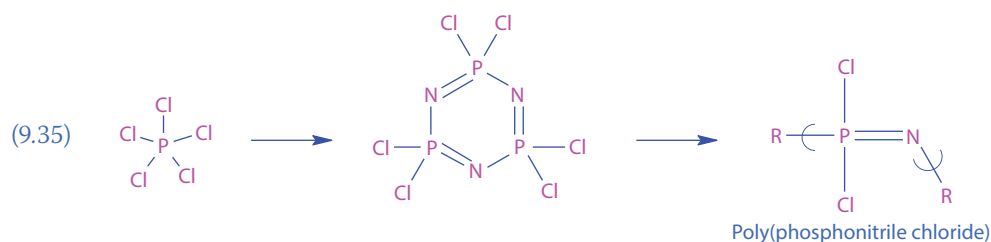
9.5 ADDITION POLYMERS

A large number of vinyl organometallic monomers have been prepared, homopolymerized, and copolymerized with classic vinyl monomers by Pittman and others. These include polymers containing Mo, W, Fe, Cr, Ir, Ru, and Co.

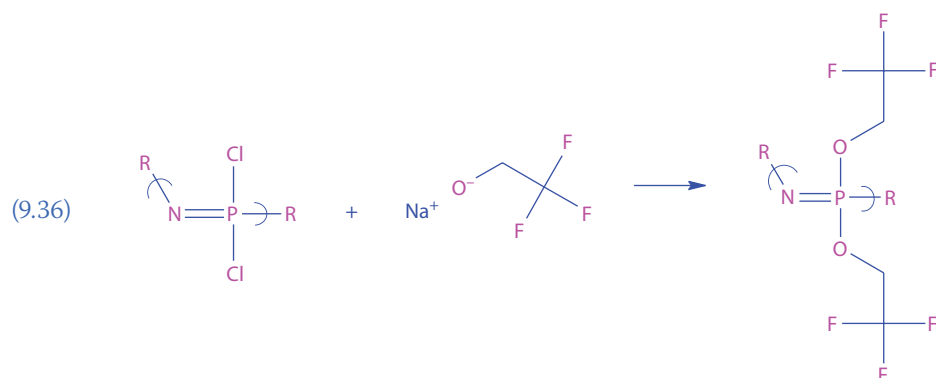
The effect that the presence of the organometallic function exerts in vinyl polymerizations is beginning to be fully understood. A transition metal may be expected, with its various readily available oxidation states and large steric bulk, to exert unusual electronic and steric effects during polymerization. The polymerization of vinylferrocene will be employed as an example. Its homopolymerization has been initiated by radical, cationic, coordination, and Ziegler–Natta initiators. Unlike the classic organic monomer styrene, vinylferrocene undergoes oxidation at the iron atom when peroxide initiators are employed. Thus, azo initiators (such as AIBN) are typically used. Here, we see one difference between an organic and an organometallic monomer in the presence of peroxide initiators. The stability of the ferricinium ion makes ferrocene readily oxidizable by peroxides, whereas styrene, for example, undergoes polymerization in their presence. Unlike most vinyl monomers, the molecular weight of polyvinylferrocene does not increase with a decrease in initiator concentration because of the unusually high chain-transfer constant for vinylferrocene. Finally, the rate law for vinylferrocene homopolymerization is the first order in initiator in benzene. Thus, intramolecular termination occurs. Mossbauer studies support a mechanism involving electron transfer from iron to the growing chain radical giving a zwitterion that terminates polymerization.

The high electron richness of vinylferrocene as a monomer is illustrated in its copolymerization with maleic anhydride, where 1:1 alternation copolymers are formed over a wide range of monomer feed ratios and $r_1 r_2 = 0.003$. Subsequently, a large number of detailed copolymerization studies have been undertaken using metal-containing vinyl monomers.

Other inorganic and metal-containing polymers have been formed using the addition approach. These include polyphosphazenes, polyphosphonitriles, and poly(sulfur nitride). Phosphonitrilic polymers have been known for many years, but since they lacked resistance to water, they were not of interest as commercial polymers. However, when the pendant chlorine groups are replaced by fluorine atoms, amino, alkoxy, or phenoxy groups, these polymers are more resistant to hydrolysis. Allcock and coworkers have pioneered these efforts. Phosphonitrile fluoroelastomers are useful throughout a temperature range of -56°C to 180°C . Phosphazene is produced by the thermal cleavage of a cyclic trimer obtained from the reaction of phosphorus pentachloride and ammonium chloride.



Amorphous elastomers are obtained when phosphazene is refluxed with nucleophiles, such as sodium trifluoroethoxide or sodium cresylate and secondary amines. Difunctional reactants such as dihydroxybenzenes (hydroquinone) produce cross-linked phosphazenes.

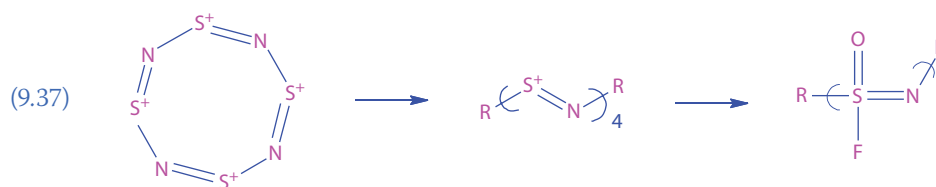


Polyphosphazenes generally exhibit very low T_g values consistent with the barriers to internal rotation being low and indicate the potential of these polymers for elastomer applications. In fact, theoretical calculations based on a rotational isomeric model assuming localized π bonding predict the lowest (400 J/mol repeating unit) known polymer barrier to rotation for the skeletal bonds for polydifluorophosphazene. Temperature intervals between T_g and T_m are unusually small and, generally, fall outside the frequently cited relationship. This behavior may be related to complications in the first-order transition generally found for organo-substituted phosphazenes and not common to other semicrystalline polymers. Two first-order transitions are generally observed for organo-substituted phosphazenes with a temperature interval from about 150°C to 200°C . The lower first-order transition can be detected using DCS, DTA, and TMA. Examination by optical microscopy reveals that the crystalline structure is not entirely lost but persists throughout the extended temperature range to a higher-temperature transition, which appears to be T_m , the true melting temperature. The nature of this transitional behavior resembles the transformation to a mesomorphic state similar to that observed in nematic liquid crystals. It appears from the relationship between the equilibrium melting temperature (heat and entropy of fusion; $T_m = H_m/S_m$) and the low value of H_m at T_m compared with the lower

transition temperature that the upper transition, T_m , is characterized by a very small entropy change. This may be due to an onset of chain motion between the two transitions leading to the small additional gain in conformational entropy at T_m . The lower transition is believed to correspond to the T_g .

Allcock and coworkers have employed polyphosphazenes in a variety of uses including the broad areas of biomedical and electrical applications. From a practical point of view, polyphosphazenes are usually soft just above the lower transition so that compression molding of films can be carried out. This suggests that the lower transition temperature represents the upper temperature for most useful engineering applications of polyphosphazenes in unmodified forms.

Sulfur nitride polymers (polythiazyls) $[-(-S=N-)-]$, which have optical and electrical properties similar to those of metals, were first synthesized in 1910. These crystalline polymers, which are superconductive at 0.25 K, may be produced at room temperature using the solid-state polymerization of the dimer (S_2N_2). A dark blue-black amorphous paramagnetic form of poly(sulfur nitride) is produced by quenching the gaseous tetramer in liquid nitrogen. The polymer is produced on heating the tetramer to about 300°C.

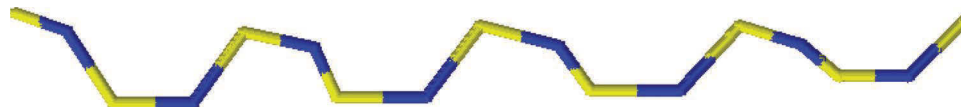


Rather than the simple up-and-down alternating structure for polythiazyls (9.38), the actual structure is more crankshaft-like (9.39) caused by the uneven bond angles of SNS (120°) and NSN (103°).

(9.38)



(9.39)



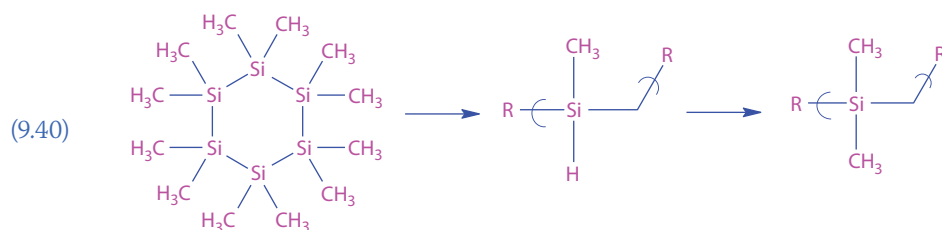
Much of the interest in the polysilanes, polygermanes, and polystannanes involves their sigma-delocalization and their sigma-pi delocalization when coupled with arenes or acetylenes. This is not unexpected since silicon exists as a covalent network similar to diamond. In exhibiting electrical conductivity, germanium and tin show more typical “metallic” bonding. Some polystannanes have been referred to as “molecular metals.”

Because of the interesting electronic and physical properties of polysilanes, a number of potential uses have been suggested including precursors of beta-SiC fibers (9.40), impregnation of ceramics, polymerization initiators, photoconductors for electrophotography, contrast enhancement layers in photolithography, deep UV-sensitive photoresists, nonlinear optical materials, and self-developing by excimer laser for deep UV exposure. The unusual absorption spectra of polysilanes have indicated potential use in a number of conducting areas.

One area of active interest in ceramics is the formation of ceramics that may contain some fiber structure. Currently, ceramics, while very strong, are very brittle. Introduction of thermally stable fiber-like materials might allow the ceramics some flexibility before cleavage. Such materials might be considered as ceramic composites where the matrix is the ceramic portion and the fibers are the thermally stable fibers. Introduction of the fibers during the ceramic-forming step is a major obstacle that must be overcome. Carbon fibers have been investigated as have been other high-temperature materials such as the polysilanes. Polysilanes are formed from the six-membered ring through extended heating at 400°C.

TABLE 9.4 Nonoxide Ceramics Produced from the Pyrolysis of Polymeric Materials

Polymer(s)	Resultant Ceramic
Poly(phosphonitrilic chlorides)	PN
Polysilanes, polycarbosilanes	SiC
Polyphenylborazole	BN
Polytitanocarbosilanes	Si-Ti-C
Polysilazanes	Si ₃ N ₄ , Si-C-N

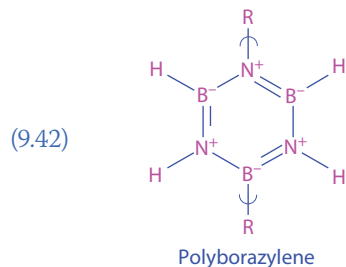
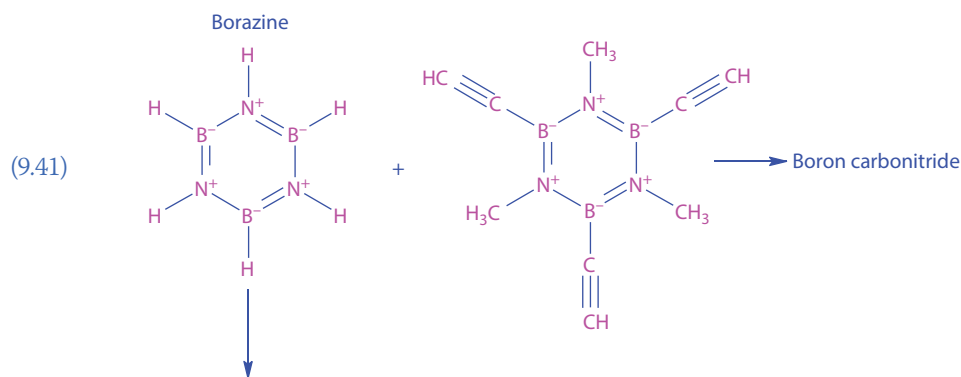


Further heating gives silicon carbide.

Table 9.4 lists a number of nonoxide ceramics that have been produced from the pyrolysis of polymers.

Boron carbonitride ceramics are formed from heating borazine with borazine derivatives (9.41).

Heating borazine yields a polymer connected by B–N bonds (9.42).



SUMMARY

1. There is a wide variety of inorganic and metal-containing polymers. The potential uses are many and include the broad areas of biomedical, electrical, optical, analytical, catalytic, building, and photochemical applications.
2. The bond strength from any combination is higher than for many traditional polymers with many having superior thermal stabilities.

3. Metal and inorganic polymers can be formed through a variety of reaction types including condensation, coordination, and addition reactions.
4. The majority of the condensation polymerizations can be considered extensions of typical Lewis acid–base reactions.
5. Polysiloxanes (silicons) offer a good combination of properties not found in organic polymers. Silicons are employed in a number of applications including antifoaming agents, lubricants, caulks, sealants, gaskets, and as biomaterials.
6. Polyphosphazenes offer unique thermal properties and have shown a number of uses in the field of electronics and medicine.
7. The number and variety of organometallic polymers and potential applications for organometallic polymers are great. Because of the high cost of production of many of these materials, uses will often be limited to applications employing minute quantities of the polymers. This is not true for many polymers containing silicon, tin, and main group materials since these are available in large quantities at reasonable cost.

GLOSSARY

Borazoles: Molecules composed of boron and nitrogen atoms.

Capping: Protecting end groups.

Carboranes: Molecules composed of carbon and boron atoms.

Coordination polymers: Polymers based on coordination complexes.

Metallocenes: Sandwich or distorted sandwich-like molecules containing generally two cyclopentadienes and a metal atom bonded to them.

Polyphosphonitrile: Polymer with a repeat unit of --P=N-- .

RTV: Room temperature vulcanization.

Siloxanes and silicones: Polymers containing --Si--O-- backbones.

EXERCISES

1. What is meant by “lost loops” in the production of silicones?
2. How could you produce a silicone with a low DP?
3. What would you estimate the solubility parameters of silicones to be?
4. Sodium silicate is water soluble (forming water glass), but silicones are water repellents. Explain the difference.
5. How might you polymerize an aqueous solution of sodium silicate?
6. How might you explain the good thermal stability of silicones?
7. Show the repeat unit for polydiethylsiloxane.
8. What are the reactants used to make phosphazenes?
9. Why would you predict that the chloro groups in phosphonitrilic polymers would be attacked by water?
10. Which phosphazene would be more flexible—one made by reaction of poly(phosphonitrilic chloride) with (a) sodium trifluoroethoxide or (b) sodium trifluorobutoxide?
11. Show the structure of borazole.
12. Since tin-containing organometallic polymers are used in marine antifouling coatings, what would you predict about their water resistance?
13. In addition to high cost, name another disadvantage of coordination polymers.
14. What is the ceiling temperature of sulfur nitride polymers?

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Inorganic Polymers

10.1 INTRODUCTION

Just as polymers abound in the world of organics, so do they abound in the world of inorganics. Inorganic polymers are the major components of soil, mountains, and sand. Inorganic polymers are also extensively employed as abrasives and cutting materials (diamond, boron carbide, silicon carbide [carborundum], aluminum oxide), coatings, flame retardants, building and construction materials (window glass, stone, Portland cement, brick, tiles), and lubricants and catalysts (zinc oxide, nickel oxide, carbon black, graphite, silica gel, alumina, aluminum silicate, chromium oxides, clays).

The first somewhat man-made, synthetic polymer was probably inorganic in nature. Alkaline silicate glass was used in the Badarian period in Egypt (about 12,000 BC) as a glaze, which was applied to steatite after it had been carved into various animal, bird, and human shapes. Frieze, a composite containing powdered quartz or steatite core covered with a layer of opaque glass, was employed from about 9000 BC to make decorative objects. The earliest known piece of regular (modern-day type) glass, dated to 3000 BC, is a lion's amulet found at Thebes and now housed in the British Museum. This is a blue opaque glass partially covered with a dark-green glass. Transparent glass appeared about 1500 BC. Several fine pieces of glass jewelry were found in Tutankhamen's tomb (ca. 1300 BC) including two bird heads of light-blue glass incorporated into the gold pectoral worn by the Pharaoh.

Because of the wide variety and great number of inorganic polymers, this chapter will focus on only a few of the more well-known inorganic polymers. Table 10.1 contains a partial listing of common inorganic polymers.

Along with the silicates that will be dealt with in (Chapter 9), there are many other inorganic polymers based on other units. One of these is the hydroxylapatite or hydroxyapatite materials that have a general formula of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, which is a member of the apatite group. Seventy percent of bone is composed of hydroxyapatite. Dental enamel is made from carbonated-calcium-deficient hydroxylapatite nanotubes. It is believed that the initial step is the production of composite nanospheres of nanocrystallite apatite and amelogenin. These then aggregate forming nanorods about 50 nm in diameter and 250 nm long. These nanorods further assemble forming elongated crystals that compose our dental enamel.

10.2 PORTLAND CEMENT

Portland cement is the least expensive, most widely used synthetic inorganic polymer. It is employed as the basic nonmetallic, nonwoody material of construction. Concrete highways and streets span our countryside and concrete skyscrapers silhouette the urban skyline. Less spectacular uses are found in everyday life as sidewalks, fence posts, and parking bumpers.

The name "Portland" is derived from the cement having the same color as the natural stone quarried on the Isle of Portland, a peninsula on the south of Great Britain. The word cement comes from the Latin word *caementum*, which means "pieces of rough, uncut stone." Concrete comes from the Latin word *concretus*, meaning "to grow together."

Common cement consists of anhydrous crystalline calcium silicates (the major ones being tricalcium silicate, Ca_3SiO_5 , and β -dicalcium silicate, Ca_2SiO_4), lime (CaO , 60%), and alumina

TABLE 10.1 Important Inorganic Polymers

Agate	Chrysotile	Kaolinite	Thomsonite
Alumina	Concrete	Mesolite	Tremolite
Aluminum oxide	Cristobalite	Mica	Tridymite
Amphiboles	Crocidolite	Montmorillonite	Valentinite
Anthophyllite	Diamond	Muscovite	Vermiculite
Arsenic selenide	Dickite	Phosphorus oxynitride	Wollastonite
Arsenic sulfide	Epistilbite	Polyphosphates (many)	Xonotlite
Asbestos	Feldspars	Quartz	Zeolites
Berlinite	Flint	Rhodonite	Zirconia
Beryllium oxide	Fuller's earth	Serpentine	
Boron nitride	Garnet	Silicon carbide	
Boron oxides	Germanium selenide	Silicon dioxides (many)	
Boron phosphate	Gibbsite	Spodumene	
Calcite	Glasses (many kinds)	Stilbite	
Carbon black	Graphite	Stishorite	
Chabazite	Imogolite	Sulfur nitride	
Chett	Jasperite	Talc	

**PICTURE 10.1** Concrete mix.

(a complex aluminum silicate, 5%) (Picture 10.1). White cement is widely used and has been studied in good detail, yet its structure and the process whereby it is formed are not completely known. This is due to at least two factors. First, its 3D arrangement of various atoms has a somewhat ordered array when a small (molecular level) portion is studied, but as larger portions are viewed, less order is observed giving only an average overall structure. This arrangement is referred to as short-range order and long-range disorder and is a good description of many 3D, somewhat amorphous inorganic and organic polymers. Thus, there exists only an average structure for the cement that varies with the amount of water and other components added, time after application (i.e., age of the cement), and source of concrete mix and location (surface or internal). Second, 3D materials are insoluble in all liquids; therefore, tools of characterization and identification that require materials to be in solution cannot be employed to assist in the structural identification of cement.

When anhydrous cement mix is added to water, the silicates react, forming hydrates and calcium hydroxide. Hardened Portland cement contains about 70% cross-linked calcium silicate hydrate and 20% crystalline calcium hydroxide.



A typical cement paste contains about 60%–75% water by volume and only about 40%–25% solids. The hardening occurs through at least two major steps (Figure 10.1). First, a gelatinous layer is formed on the surface of the calcium silicate particles. The layer consists mainly of water with some calcium hydroxide. After about 2 hours, the gel layer sprouts fibrillar outgrowths that radiate from each calcium silicate particle. The fibrillar tentacles increase in number and length, becoming enmeshed and integrated. The lengthwise growth slows, with the fibrils now joining up sideways, forming striated sheets that contain tunnels and holes. During this time, calcium ions are washed away from the solid silicate polymeric structures by water molecules and react further, forming additional calcium hydroxide. As particular local sites become saturated with calcium hydroxide, calcium hydroxide itself begins to crystallize, occupying once vacant sites and carrying on the process of interconnecting about and with the silicate “jungle.”

In spite of attempts by the silicate and calcium hydroxide to occupy all of the space, voids are formed, probably from the shrinkage of the calcium hydroxide as it forms a crystalline matrix. (Generally crystalline materials have higher densities than amorphous materials; thus, a given amount will occupy less volume, leaving some unfilled sites.) Just as a chain is no stronger than its weakest link, so also is cement no stronger than its weakest sites, that is, its voids. Much current research concerns attempts to generate stronger cement with the focus on filling these voids. Interestingly, two of the more successful cement–void–fillers are also polymers—dextran, a polysaccharide, and polymeric sulfur.

Table 10.2 shows a typical concrete mix. The exact amounts may vary by as much as 50% depending on the intended use and preference of the concrete maker.

The manufacture of Portland concrete consists of three basic steps—crushing, burning, and finish grinding. As noted before, Portland cement contains about 60% lime, 25% silicates, and 5% alumina with the remainder being iron oxides and gypsum. Most cement plants are located near limestone (CaCO_3) quarries since this is the major source of lime. Lime may also come from

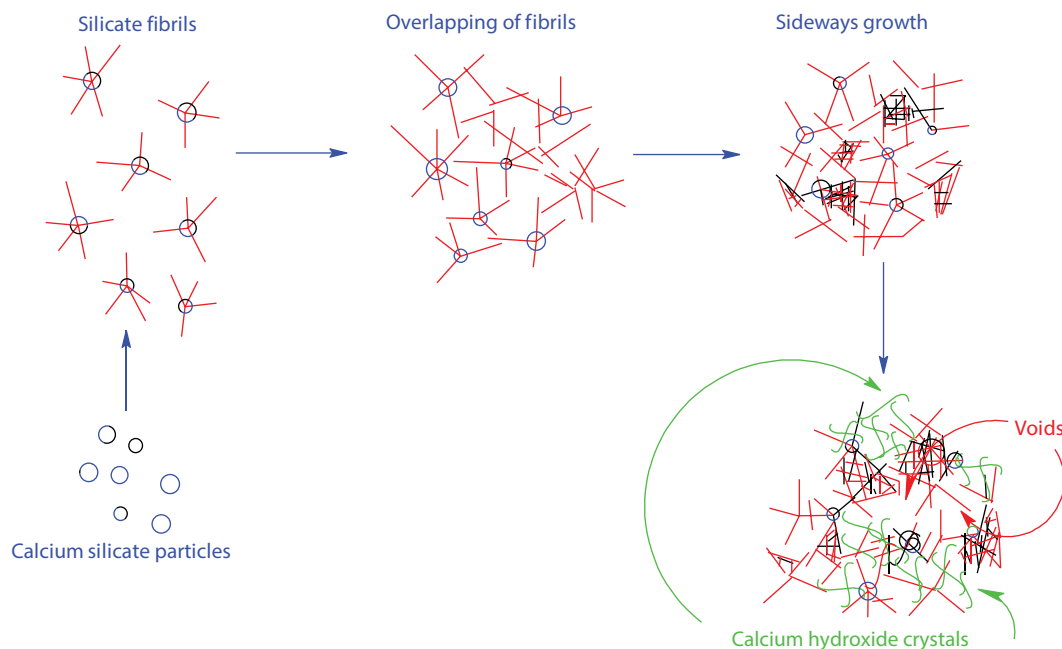


FIGURE 10.1 Steps in the hardening of Portland cement.

TABLE 10.2 Sample Concrete Mix

Material	Amount	
	By Volume	By Weight
Portland cement	90–100 lb (1 ft ³)	90–100 lb (40–50 kg)
Water	5.5 gal	45 lb (20 kg)
Sand	2 ft ³	200 lb (90 kg)
Gravel (small rocks)	3 ft ³	250 lb (120 kg)

**PICTURE 10.2** Concrete and metal skyline buildings, Dubai, UAE.

oyster shells, chalk, and a type of clay called marl. The silicates and alumina are derived from clay, silicon sand, shale, and blast furnace slag.

Concrete is the material used to build roads, skyscrapers (Picture 10.2), highways, bridges, and many other structures. It is relatively inexpensive, long lasting, easy to work with, and strong.

10.3 OTHER CEMENTS

There are a number of cements specially formulated for specific uses. *Air-entrained concrete* contains small air bubbles formed by the addition of soaplike resinous materials to the cement or to the concrete when it is mixed. The bubbles permit the concrete to expand and contract

(as temperature changes) without breaking (since the resistance of air to changes in the concrete volumes is small). *Lightweight concrete* may be made through the use of lightweight fillers such as clays and pumice in place of sand and rocks or through the addition of chemical foaming agents that produce air pockets as the concrete hardens. These air pockets are typically much larger than those found in air-entrained concrete.

Reinforced concrete is made by casting concrete about steel bars or rods. Most large cement-intensive structures such as bridges and skyscrapers employ reinforced concrete. *Prestressed concrete* is typically made by casting concrete about steel cables stretched by jacks. After the concrete hardens, the tension is released, resulting in the entrapped cables compressing the concrete. Steel is stronger when tensed, and concrete is stronger when compressed. Thus, prestressed concrete takes advantage of both of these factors. Archways and bridge connections are often made from prestressed concrete.

Concrete masonry is simply the name given to the cement building blocks employed in the construction of many homes, and it is simply a precast block of cement, usually with lots of voids (Picture 10.3). *Precast concrete* is concrete that is cast and hardened before it is taken to the site of construction. Concrete sewer pipe, wall panels, beams, grinders, and spillways are all examples of precast cements.

The cements cited earlier are all typically derived from Portland cement. The following are non-Portland cements.

Calcium-aluminate cement has a much higher percentage of alumina than does Portland cement. Furthermore, the active ingredients are lime, CaO , and alumina. In Europe it is called melted or fused cement. In the United States, it is manufactured under the trade name Lumnite. Its major advantage is its rapidity of hardening, developing high strength within a day or two.

Magnesia cement is largely composed of magnesium oxide (MgO). In practice, the magnesium oxide is mixed with fillers and rocks and an aqueous solution of magnesium chloride. This cement sets up (hardens) within 2–8 hours and is employed for flooring in special circumstances.

Gypsum, or hydrated calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), serves as the basis of a number of products including plaster of Paris (also known as molding plaster, wall plaster, and finishing plaster). The ease with which plaster of Paris and other gypsum cements can be mixed and cast (applied) and the rapidity with which they harden contribute to their importance in the construction field as a major component for plaster wall boards. Plaster of Paris' lack of shrinkage in hardening accounts for its use in casts. Plaster of Paris is also employed as a dental plaster, pottery plaster,



PICTURE 10.3 Concrete building blocks.

and molds for decorative figures. Unlike Portland cement, plaster of Paris requires only about 20% water and dries to the touch in 30–60 minutes giving maximum strength after 2–3 days. Portland cement requires several weeks to reach maximum strength.

10.4 SILICATES

Silicon is the most abundant metallike element in Earth's crust. It is seldom present in pure elemental form, but rather is present in a large number of polymers largely based on the polycondensation of the orthosilicate anion, SiO_4^{-4} as illustrated in the following:



The number listed with each product corresponds with the “geometric ID number” given in Table 10.3 and the “structural geometry” given in Table 10.3 and depicted in Figure 10.2.

Each of these steps is based on a tetrahedral silicon atom attached to four oxygen atoms. The complexity and variety of naturally occurring silicates is due to two major factors. First, the ability of the tetrahedral SiO_4^{-4} unit to be linked together often giving polymeric structures. Second, the substitution of different metal atoms of the same approximate size as that of Si often occurs giving many different materials.

In the structures cited in Table 10.3, except for pure SiO_2 , metal ions are required for overall electrical neutrality. These metal ions are positioned in tetrahedral, octahedral, etc., positions in the silicate-like lattice. Sometimes they replace the silicon atom. Kaolinite asbestos (Figure 10.3) has aluminum substituted for silicon in the Gibbsite sheet.

Further, sites for additional anions, such as the hydroxyl anion, are available. In ring, chain, and sheet structures, neighboring rings, chains, and sheets are often bonded together by metal ions held between the rings. In vermiculite asbestos, the silicate sheets are held together by non-silicon cations.

For sheet-layered compounds, the forces holding together the various sheets can be substantially less than the forces within the individual sheets. Similar to graphite, such structures may be easily cleaved parallel to the sheets. Examples of such materials are mica, kaolinite, and talc.

Bonding occurs through a combination of ionic and covalent contributions just as are present in organic polymers except that the ionic character is a little higher. “Back-bonding” from electrons associated with the oxygen to vacant orbitals in the silicon (or other tetrahedral metal atom) occurs giving the silicon–oxygen linkages some double- or pi-bond character.

TABLE 10.3 Inorganic Polymeric Silicates as a Function of Common Geometry

Geometric ID Number (Text)	Basic Geometric Unit	Structural Geometry (Figure 10.2)	General Silicate Formula ^a	Examples ^a
1	Tetrahedron	A	SiO_4^{-4}	Granite olivine- $(\text{Mg,Fe})_2\text{SiO}_4$ Fosterite- Mg_2SiO_4 Topaz
2	Double tetrahedron	B	$\text{Si}_2\text{O}_7^{-6}$	Akermanite- $\text{Ca}_2\text{MgSi}_2\text{O}_7$
3	Triple ring	C	$\text{Si}_3\text{O}_9^{-6}$	Wollastonite
4	Tetra ring	D	$\text{Si}_4\text{O}_{12}^{-8}$	Neptunite
5	Six ring	E	$\text{Si}_6\text{O}_{18}^{-12}$	Beryl- $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$
6a	Linear Chain	F	$\text{Si}_4\text{O}_{12}^{-8}$	Augite, enstatite- MgSiO_3 Diopside- $\text{CaMg}(\text{SiO}_3)_2$ Chrysotile- $\text{Mg}_6\text{Si}_4\text{O}_{11}(\text{OH})_6$
6b	Double-stranded ladder	G	$\text{Si}_4\text{O}_{11}^{-6}$	Hornblende
7	Parquet (layered)	H	$\text{Si}_4\text{O}_{10}^{-4}$	Talc- $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ Mica- $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ Kaolinite- $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Condensed) silicic acid- $\text{H}_2\text{Si}_2\text{O}_5$
8	Network	I	SiO_2	Quartz, feldspar (orthoclase)- KAlSi_3O_8

^a The formulas given are for the most part simplified.

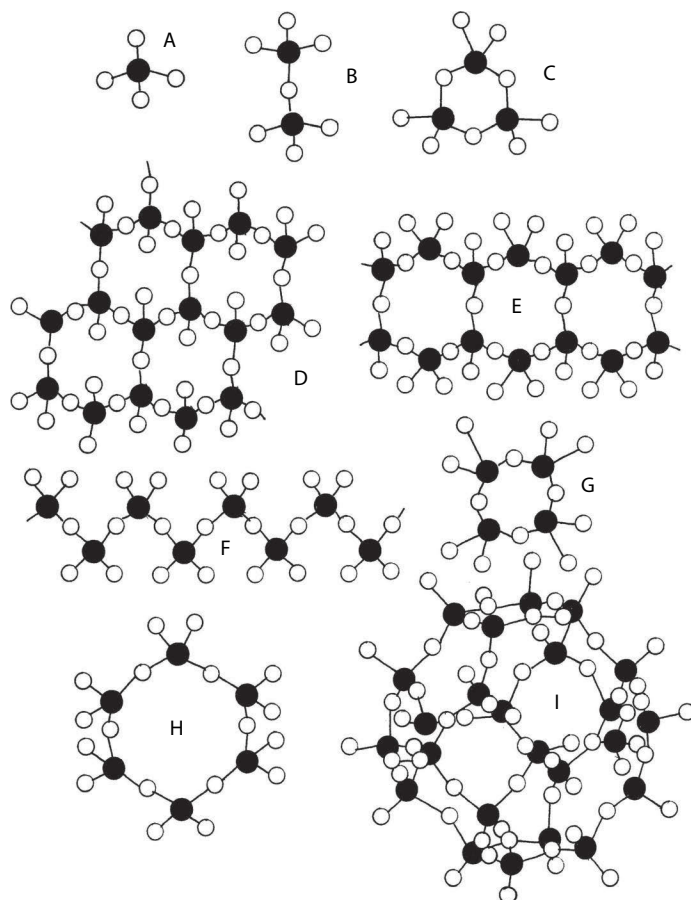


FIGURE 10.2 General silicate structures. Letters are associated with Table 10.3, third column.

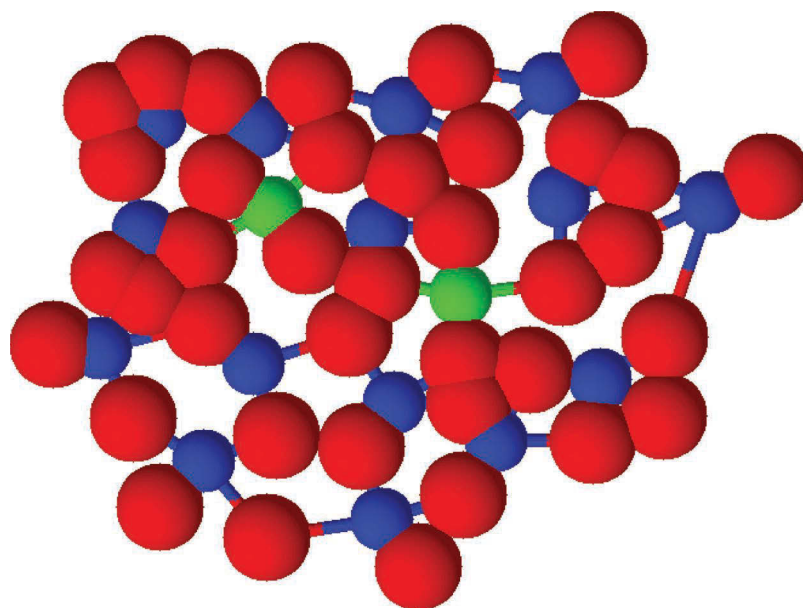


FIGURE 10.3 Two-dimensional representation of a multicomponent silicon dioxide–intense glass where the red spheres are oxygen, blue spheres are silicon, and the off-color green spheres are an impurity cation.

As noted before, cations other than silicon may occupy the tetrahedral centers. A major factor in predicting which cations will be found to substitute for silicon is ionic size. In general, cations whose size is about 0.03–0.1 nm are the best candidates. Si^{+4} has an ionic radius of about 0.041 nm. Cations such as Fe^{+2} (ionic radius = 0.07 nm), Al^{+3} (0.05 nm), Ca^{+2} (0.1 nm), and Mg^{+2} (0.065 nm) are most often found in silicate-like structures and meet this requirement.

Most silicate-like polymers can be divided into three major classes—the network structures based on a 3D tetrahedral geometry (such as quartz), layered geometries with stronger bonding occurring within the “two-dimensional” layer (such as talc), and linear structures.

10.4.1 NETWORK

Quartz is an important network silicate (Section 10.7). A number of additional tetrahedral silicate-like materials possess some AlO_4 tetrahedra substituted for the SiO_4 tetrahedra. Such structures offer a little larger “hole” in comparison to the entirely SiO_4 structures allowing alkali and alkaline–earth cations to be introduced. Feldspar (orthoclase) is such a mineral. The aluminosilicate networks are almost as hard as quartz. For feldspar and other tetrahedral networks, the number of oxygen atoms is twice the summation of silicon and other MO_4 cations.

The feldspars are widely distributed and comprise almost two-thirds of all igneous rocks. Orthoclase and albite, $\text{NaAlSi}_3\text{O}_8$, are feldspars where one-fourth of the silicon atoms are replaced by aluminum and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, has one-half of the silicon atoms replaced by aluminum. Because the ionic radius of Na^+ (0.095 nm) and Ca^{+2} (0.1 nm) are about the same, solid solutions are often formed between albite and anorthite. Good stones of albite and orthoclase are known as moonstones.

Some of the network structures exhibit a framework sufficiently “open” to permit ions to move in and out. The zeolite minerals used for softening water are of this type.

Ultramarines are 3D cage-like structures. They differ from feldspars and zeolites because of the large spaces within the structures that can contain cations and anions but no water illustrating a natural “buckyball-like” structure and cavity and a diversity of environment between the internal cage and external. Ultramarines can act as ion exchangers for both anions and cations. The blue color of ultramarines is due to the presence of the S_3^- ion although a yellow ion S_2^- also exists in the same structure.

10.4.2 LAYER

Layered structures typically conform to the approximate composition $\text{Si}_4\text{O}_{10}^{-4}$ or $\text{Si}_2\text{O}_5^{-2}$. For most of these, three of the oxygen atoms of each tetrahedron are shared by other tetrahedra, and the fourth oxygen is present on one side of the sheet.

In talc and kaolinite the layers are neutral. Thus, the layers slide over one another easily imparting to these minerals a softness and ease in cleavage. In other minerals the layers are charged and held together by cations. In mica, the aluminosilicate layers are negatively charged and cations, generally K^+ , are present between the layers giving the entire system of layers electronic neutrality. The ionic attractive forces between the layers result in mica (Picture 10.4) being much harder than talc and kaolinite. Even so, these inter-sheet bonding forces are less than the “within-the-sheet” bonding forces permitting relatively easy and clean cleavage of mica. Mica is used as an insulator for furnaces and electric equipment. Montmorillonite is an important ingredient in soils and is employed industrially as a catalyst in the conversion of straight-chain hydrocarbons to more branched hydrocarbons and more recently as a sheet or clad material in the manufacture of tires.

Vermiculites are formed by the decomposition of mica. They contain layers of water and magnesium ions in place of the potassium ions. When heated to 800°C – 1100°C , vermiculite expands because of the conversion of the water to a gas. The expanded vermiculite has a low thermal conductivity and density and is used as a thermal and sound barrier and as an aggregate in lightweight concrete. It is also used as a moisture-retaining soil conditioner in planting.

A number of clays are layered silicate-like materials. Most clays contain finely divided quartzes, micas, and feldspars. Iron oxide-rich clays are employed to make pottery and terra cotta articles. Clays containing iron oxide and sand are used to make bricks and tiles. Clays rich in calcium and magnesium carbonate are known as marls and are used in the cement industry (Section 10.2).

Kaolinite is the main constituent in china clay used to make porcelain. The layers are largely held together by van der Waals forces. Bentonite is used in cosmetics, as a filler for soaps, and as a plasticizer, and it is used in drilling muds as a suspension stabilizer. Bentonite and kaolinite clays are used, after treatment with sulfuric acid to create acidic surface sites, as petroleum cracking catalysts. Asbestos also has a layered structure (Section 10.8).



PICTURE 10.4 Mica-shiny sheetlike material on the granite rock.

10.4.3 CHAIN

Both single- and double-stranded chains are found. The most important members of single chains are the pyroxenes and include diopside. The most important double-chained minerals are the amphiboles. Some of these contain hydroxyl and fluoride ions, bonded directly to the metal cation and not to the silicon atom.

Jade, which has been valued in carving by eastern Asians for centuries, is generally one of two minerals—pyroxene or jadeite, $\text{NaAl}(\text{SiO}_3)_2$, and the amphibole nephrite, $\text{Ca}_2(\text{Fe}^{+2}$ and/or $\text{Mg}^{+2})_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$. X-Ray diffraction has shown the presence of triple chains in nephrite.

Because the interchain bonding is weaker than the Si–O backbone bonding, these chain structures can generally be easily cleaved between the chains.

Several amphiboles are fibrous and fibers from them can be processed to give heat-insulating materials. Among these are tremolite and crocidolite. These minerals are also used as fibers in composites.

10.5 SILICON DIOXIDE (AMORPHOUS)

Silicon dioxide (SiO_2) is the major repeating general formula for the vast majority of rock, sand, and dirt found about us and for the material we refer to as glass (Picture 10.5). The term glass can refer to many materials, but here we will use the ASTM definition that glass is an inorganic product of fusion that has been cooled to a rigid condition without crystallization. In this section, silicate glasses, the common glasses for electric light bulbs, window glass, drinking glasses, glass bottles, glass test tubes and beakers, and glass cookware, will be emphasized.

Glass has many useful properties, as listed in Table 10.4. It ages (changes chemical composition and physical property) slowly, typically retaining its fine optical and hardness-related properties for centuries. Glass is referred to as a supercooled liquid or a very viscous liquid. Indeed, it is a slow-moving liquid as attested to by sensitive measurements carried out in some laboratories. Concurrent with this is the observation that the old stained-glass windows adorning European cathedrals are a little thicker at the bottom of each small, individual piece than at the top of the piece. For most purposes though, glass can be treated as a brittle solid that shatters on sharp impact.



PICTURE 10.5 Sand dunes near Hatta, UAE.

TABLE 10.4 General Properties of Silicate Glasses

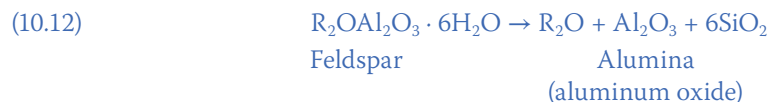
High transparency to light	Permanent (long-term) transparency
Hard	Scratch-resistant
Chemically inert	Low thermal expansion coefficient
Good electrical insulator	High sparkle
Good luster	Low porosity
Good ease of reforming	Easily recyclable
(Relatively) inexpensive	Available in large amounts

Glass is mainly silica sand (SiO_2) and is made by heating silica sand and powdered additives together in a specified manner and proportion much as a cake is baked, following a recipe that describes the items to be included, amounts, mixing procedure (including sequence), oven temperature, and heating time. The amounts, nature of additives, etc., all affect the physical properties of the final glass.

Typically cullet, recycled or waste glass (5%–40%), is added along with the principle raw materials (mostly SiO_2). The mixture is thoroughly mixed and then added to a furnace where the mixture is heated to near 1500°C to form a viscous, syrup-like liquid. The size and nature of the furnace corresponds to the glasses' intended uses. For small, individual items, the mixture may be heated in a small clay (refractory) pot.

Most glass is melted in large (continuous) tanks that can melt 400–600 metric tons a day for production of different glass products. The process is continuous with the raw materials fed into one end as molten glass is removed from the other end. Once the process (called a campaign) is begun, it is continued indefinitely, night and day, often for several years until the demand is met or the furnace breaks down.

A typical window glass will contain 95%–99% silica sand with the remainder being soda ash (Na_2CO_3), limestone (CaCO_3), feldspar, and borax or boric acid along with the appropriate coloring and decolorizing agents, oxidizing agents, etc. As noted previously, 5%–40% by weight of crushed cullet is also added. The soda ash, limestone, feldspar, and borax or boric acid all form oxides as they are heated, which become integrated into the silicon structure (10.10) through (10.13):



The exact structure varies according to the ingredients and actual processing conditions. As in the case of Portland cement, glass is a 3D array that offers short-range order and long-range disorder—it is amorphous offering little or no areas of crystallinity. The structure is based on the silicon atoms existing in a tetrahedral geometry with each silicon atom attached to four oxygen atoms, generating a 3D array of inexact tetrahedra. Thus, structural defects occur, due in part to the presence of impurities such as Al, B, and Ca, intentionally or unintentionally introduced. These impurities encourage the glass to cool to an amorphous structure since the different-sized impurity metal ions and different charges on the metal ions, disrupt the rigorous space requirement necessary to allow crystal formation. Figure 10.3 is an illustration of this situation and contains two atoms of impurity.

Processing includes shaping and pretreatments of the glass. Since shaping may create undue sites of amorphous structure, most glass objects are again heated to near their melting point. This process is called “annealing.” Since many materials tend to form more ordered structures when heated and recooled slowly, the effect of annealing is to “heal” sites of major dissymmetry. It is important to heal these sites since they represent preferential locations for chemical and physical attack such as fracture.

Four main methods are employed for shaping glass. They are drawing, pressing, casting, and blowing. Drawing is employed for shaping flat glass and glass tubing and for creating fibrous glass. Most flat glass is shaped by drawing a sheet of molten glass (heated so it can be shaped but not so it freely flows) onto a tank of molten tin. Since the glass literally floats on the tin, it is called “float glass.” The temperature is carefully controlled. The glass from the float bath typically has both sides quite smooth with a brilliant finish that requires no polishing.

As noted earlier, annealing encourages the removal of sites of stress and strain. Slow cooling results in a glass with more crystallinity, which is stronger but more brittle. “Tempering” is the name given when the glass is rapidly cooled, resulting in an amorphous glass that is weaker but less brittle. The correlation between crystallinity, rate of cooling, and brittleness is demonstrated by noting that older window glass exposed to full sun for years is more brittle and more easily shattered since the sunlight raises the temperature sufficiently to permit small molecular movements (though even in full sunlight the glass is not near the temperature required for ready movement) and over the years gives a glass with small regions of greater order.

Silicon-based glasses account for almost all of the glasses manufactured. Silica is finely ground silica sand. Yet most sand is unsuitable for general glassmaking due to the presence of excessive impurities. Thus, while sand is plentiful, sand that is useful for the production of glass is much less common. In fact, the scarcity of large deposits of glass sand is one major reason for the need to recycle glass items. The second major reason is associated with the lowered energy requirements for glass to be made molten again for reshaping compared with a virgin glass mixture, that is, culled glass becomes molten at lower temperatures than virgin glass.

10.5.1 KINDS OF GLASS

The types and properties of glass can be readily varied by changing the relative amounts and nature of ingredients. “Soda-lime glass” is the most common of all glasses accounting for about 90% of glass made. Window glass, glass for bottles, etc., are all soda-lime glass. Soda-lime glass (75% silica, 15% soda [sodium oxide], 9% lime [calcium oxide], and the remaining 4% minor ingredients) has a relatively low softening temperature and low thermal shock resistance limiting its high-temperature applications.

Vycor, or 96% silicon glass, is made using silicon and boron oxide. Initially the alkali–borosilicate mixture is melted and shaped using conventional procedures. The article is then heat-treated, resulting in the formation of two separate phases—one that is high in alkalis and boron oxide and the other containing 96% silica and 3% boron oxide. The alkali–boron oxide phase is soluble in strong acids and is leached away by immersion in hot acid. The remaining silica–boron oxide phase is quite porous. The porous glass is again heated to about 1200°C, resulting in a 14% shrinkage due to the remaining portions filling the porous voids. The best variety is “crystal” clear and called “fused quartz.” The 96% silica glasses are more stable and exhibit higher melting points (1500°C) than soda-lime glass. Crucibles, ultraviolet filters, range burner plates, induction furnace linings, optically clear filters and cells, and super heat-resistant laboratory ware are often 96% silicon glass.

Borosilicate glass contains about 80% silica, 13% boric oxide, 4% alkali, and 2% alumina. It is more heat-shock-resistant than most glasses due to its unusually small coefficient of thermal expansion (typically between 2 and 5×10^{-6} cm/cm/°C; for soda-lime glass it is 8 to 9×10^{-6} cm/cm/°C). It is better known by such trade names as Kimax and Pyrex. Bakeware and glass pipelines are often borosilicate glass.

Lead glasses (often called heavy glasses) are made by replacing some or all of the calcium oxide by lead oxide (PbO). Very high amounts of lead oxide can be incorporated—up to 80%. Lead glasses are more expensive than soda-lime glasses, and they are easier to melt and work with.



PICTURE 10.6 Stained-glass window about 150 years old that was over the front door of a bank in Billings, OK.

They are more easily cut and engraved, giving a product with high sparkle and luster (due to the high refractive indexes). Fine glass and tableware are often lead glass.

Silicon glass is made by fusing pure quartz crystals or glass sand (impure crystals), and it is typically about 99.8% SiO_2 . It is high melting and difficult to fabricate.

Colored or stained glass has been made for thousands of years, first by Egyptians and later by Romans (Picture 10.6). Color is typically introduced by addition of transition metals and oxides. Table 10.5 contains selected inorganic colorants and the resulting colors. Because of the high clarity of glass, a small amount of coloring agent goes a long way. One part of cobalt oxide in 10,000 parts of glass gives an intense blue glass. The most well-known use for colored glass is the construction of stained-glass windows. In truth, there are many other uses such as industrial color filters and lenses.

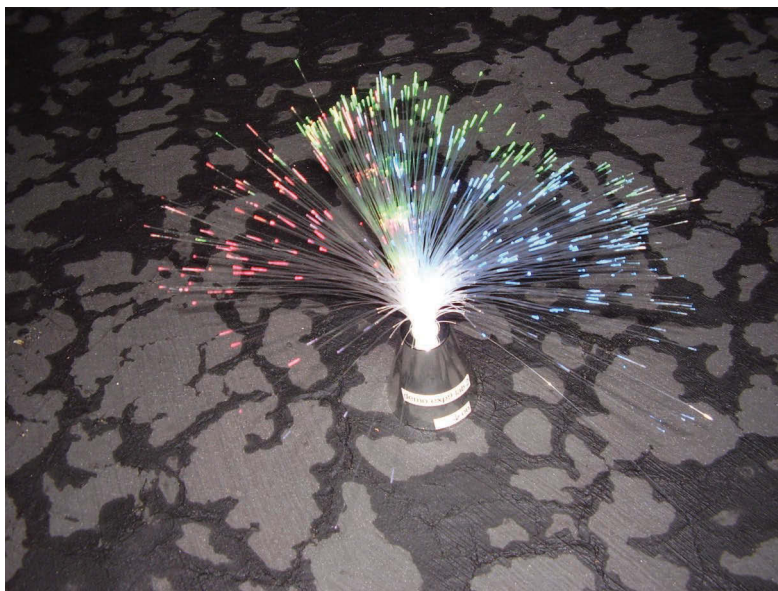
Glazes are thin, transparent coatings (colored or colorless) fused on ceramic materials. *Vitreous enamels* are thin, normally opaque or semiopaque, colored coatings fused on metals, glasses, or ceramic materials. Both are special glasses but can contain little silica. They are typically low melting and often are not easily mixed in with more traditional glasses.

Optical fibers can be glass fibers that are coated with a highly refractive polymer coating such that light entering one end of the fiber is transmitted through the fiber (even around corners as within a person's stomach), emerging from the other end with little loss of energy (Picture 10.7). These optical fibers can also be made to transmit sound and serve as the basis for transmission of television and telephone signals over great distances through cables.

There are many silica-intensive fibers lumped together such as “*fibrous glass*” or “*fiber-glass*.” A general-purpose fiberglass may contain silica (72%), calcium oxide (9.5%), magnesium

TABLE 10.5 Colorants for Stained Glass

Colorant	Color	Colorant	Color
Nickel(II) oxide	Yellow to purple	Calcium fluoride	Milky white
Cobalt(II) oxide	Blue	Iron(II) compounds	Green
Iron(III) compounds	Yellow	Copper(I) oxide	Red, blue, or green
Tin(IV) oxide	Opaque	Manganese(IV) oxide	Violet
Gold(III) oxide	Red		



PICTURE 10.7 Optical fibers where a light in the base is transferred through the fibers to the end of the fibers.

oxide (3.5%), aluminum oxide (2%), and sodium oxide (13%). The fibers are produced by melting the “glass mixture” with the molten glass drawn through an orifice. The filaments are passed through a pan containing sizing solution onto a winding drum. The take-up rate of the filament is more rapid than the exit rate from the orifice acting to align the molecules and draw the fibers into thinner filaments. Thus, a fiber forced through a 0.1 cm orifice may result in filaments of 0.0005 cm diameter. This drawing increases the strength and flexibility of the fiberglass. Applications of fiberglass include insulation (Picture 10.8) and use in composites.

Table 10.6 contains a listing of major glass-producing companies in the United States.

Optical glass for eyeglass lenses and camera lenses is typically soda-lime glass that is highly purified so that it is highly transmissive of light. Today, there exists many other special glass that are important in today’s society such as laser glasses, photosensitive glass, photochromic windows and eyeglass glass, invisible glasses, and radiation absorbing glass.



PICTURE 10.8 Fiberglass insulation.

TABLE 10.6 Leading U.S. Glass Companies

Owen-Illinois, Inc.	PPG Industries, Inc.
Corning Glass Works	Owens-Corning Fiberglass Corporation
Libbey-Owens-Ford Company	

10.5.2 SAFETY GLASS

Safety glass is defined as “glass” that diminishes the threat of injuries and robberies as a result of impacts, distortion, or fire.

In 1905, British inventor John C. Wood was working with cellulose and developed a method to adhere glass panes using celluloid as the adhesive. Wood’s version of shatter-resistant glass was produced under the brand name Triplex since it consisted of outer layers of glass with an inner layer of celluloid polymer.

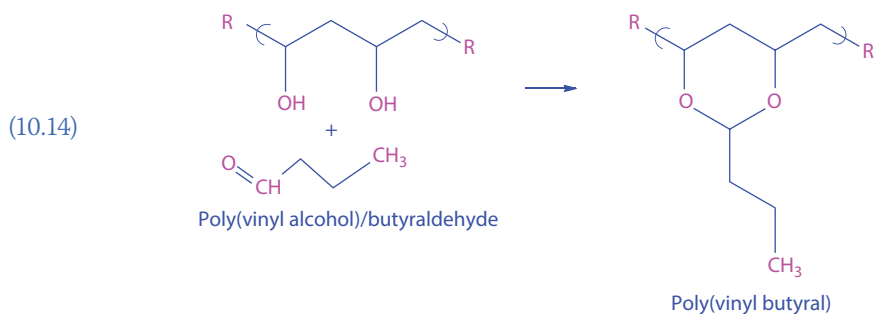
About the same time, Edouard Benedictus, a French chemist, was climbing a ladder to get chemicals from a shelf and accidentally (another discovery due to an accident) knocked a glass flask onto the floor. He heard the flask shatter but when he looked at the broken flask, the broken pieces hung together instead of breaking into many pieces and scattering over the floor. Benedictus learned from his assistant that the flask had recently held a solution of cellulose nitrate. The solution of cellulose nitrate dried to give a thin film that was transparent, so the flask was set aside as a “cleaned” flask. It was this thin film that coated the inside of the flask that held together the broken pieces. The film was formed on evaporation of cellulose nitrate prepared from cellulose and nitric acid.

Shortly after the laboratory accident, he read about a girl who had been badly cut from flying glass resulting from an automobile accident. Later he read about other people being cut by flying glass in automobile accidents. He remembered the flask that did not splinter into small pieces when broken because of the cellulose nitrate coating. He experimented with placing cellulose nitrate between sheets of glass, using pressure to help adhere the glass with the cellulose nitrate. By 1909, Benedictus had patented the material.

Prior to its use in windshields, safety glass found its initial major application as the lenses for gas masks during World War I. Manufacturers found it easy to work with so that the technology and ability to manufacture safety glass windshields came easily.

As automobiles became more common, so did the hazards of mud, rocks, etc., so that by 1904, windshields were introduced. These first windshields could be folded and/or moved if they became blocked by excessive mud. While the usefulness of the windshield was abundantly obvious, drivers found that they were dangerous during a wreck cutting passengers, drivers, and passersby alike. Because the drivers were believed to be primarily responsible for automobile safety, most manufactures were slow to adopt safety glass. In 1919, Henry Ford addressed the windshield problem by having safety glass windshields on his automobiles.

This safety glass turned yellow after several years of exposure to light. The bonding layer was replaced in 1933 by cellulose acetate, made from the reaction of cotton with acetic acid. By 1939, this was replaced by poly(vinyl butyral) (PVB) still in use today as the adhesive placed between sheets of glass to produce laminated safety glass. This is one of a very few modern-use materials that has retained the same basic materials for over 70 years.



PVB is made from poly(vinyl alcohol), which itself is made from poly(vinyl acetate) because the monomer vinyl alcohol does not exist (10.14).

Today, safety glass is divided into three general categories, laminated safety glass, tempered safety glass, and armed glass. *Tempered safety glass* is made by heating the glass to its melting point, about 700°C, and then cooling it rapidly by blowing cold air onto its surfaces. The effect is similar to the production of stressed concrete where the concrete is allowed to harden under stress giving a stronger concrete. In the case of glass, when it is rapidly cooled, a structure is locked in that it produces extra stress on the glass structure making it stronger. As the glass is cooled, the surfaces harden first locking in the overall glass volume. As the center cools, it forces the surfaces and edges into compression. With appropriate rapid cooling, the glass not only is stronger but, when shattered, also produces granulates rather than sharp cutting shards. The typical force necessary to break tempered glass is about four times that required to shatter ordinary glass of the same thickness.

While the front “windshield” is made of safety glass, the remainder of the automotive glass windows is generally made from tempered glass. Tempered glass is also used for commercial building doors and windows, sidelights, patio-door assemblies, storm doors, shower and tub enclosures, refrigerator, oven, and stove shelves, and fireplace screens.

Armed glass is most commonly used as roofing on factory buildings. It is a glass that has a built-in metal grill that strengthens the glass. The metal grill is often like chicken wire in appearance. The glass breaks similar to regular glass, but the wire mesh helps hold it into place. The visibility is reduced because of the presence of the metal mesh.

Laminated glass is used in automobiles and often used for added protection in windows, balconies, or sloping glass roofs. The laminated glass resists breakage in comparison to ordinary glass because the PVB inner layer(s) helps dampen sharp blows. Even so, laminated glass is more easily cracked than tempered glass. But it is harder to pierce than tempered glass because of the PVB inner layer(s). Another difference is that laminated glass can be cut, sawn, or drilled whereas tempered glass cannot. The PVB film also has ultraviolet-screening properties reducing discoloration of objects placed behind the safety glass. It also acts to dampen sound for additional soundproofing.

Laminated safety glass is available in different thicknesses depending on the number of PVB-glass layers. *Bullet-resistant glass* is one use for thick, multilayer laminated safety glass. The laminated construction allows the multilayer assembly to have some additional flexibility with the multiple layers yielding, allowing the PVB layers to absorb some of the energy of the bullet. The plastic layers help hold the shattered glass fragments together aiding in retaining a restraining barrier. Such glass is used in bank teller windows, and in windshields for aircraft, tanks, and special automobiles and trucks. Many of these applications are being replaced by various high-strength plastics.

The ability to resist bullets and blasts is increased by increasing the number of layers of laminated safety glass. Such increases give an increased glass thickness and weight. So there is a trade-off between expected abuse and practicality.

10.5.3 NEW APPLICATIONS OF GLASS

Glass is a complex material and in that complexity is a possibility to use it in many different ways. Here we will briefly introduce some of the newer applications for glass. Remember that glass is largely silicon dioxide—it can be readily available and inexpensive; it is generally scratch resistant, somewhat strong, and flexible; and it has good optical transparency. This combination allows many varied applications for glass. Glass is somewhat tunable to give products with varying properties through introduction of “impurities,” additives, and surface treatments.

Glass can be fashioned into sheets of varying thicknesses. Recently, Corning has introduced a thin flexible glass it calls Willow Glass because of this flexibility. The glass can be produced as thin as 100 μm thick, about the thickness of thin paper. It is being used in place of plastic on computer notebooks and tablets and on smartphones. Corning uses ion exchange to increase toughness and scratch resistance of its sodium aluminosilicate glass producing what they call its Gorilla Glass line. Larger potassium ions replace smaller sodium ions creating compressive forces that toughen the surface by closing and discouraging formation of pathways for fracture propagation.

Saxon Glass Technologies uses a similar toughening procedure to produce tougher glass cartridges for injectors used for self-administration of epinephrine to treat life-threatening allergic reactions.

Mo-Sci produces special microspheres containing a radioactive yttrium aluminosilicate, YAS, glass used to destroy malignant tumors.

When a person sustains a wound, fibrinogen and thrombin react forming a polymerized mesh that clots the wound site protecting it from unwanted microbes and aiding in the healing process. Persons with compromised healing processes, such as those with poor circulation, diabetes, vascular diseases, etc., are often unable to heal properly. Scientists at Mo-Sci have also developed DermaFuse that is a cotton-like bioactive borate glass that can be placed within the wound acting to assist the healing process.

In density, metal-free ceramics based on glass have been developed that are used as crown and filling materials. Materials based on leucite, KAlSi_2O_6 , are used to fabricate crowns and inlays. Lithium disilicate, $\text{Li}_2\text{Si}_2\text{O}_6$, because of added flexibility in comparison to leucite, is now used in bridgework. Fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, is also used in dentistry because needlelike crystals that are formed by the material result in translucency similar to that of natural teeth.

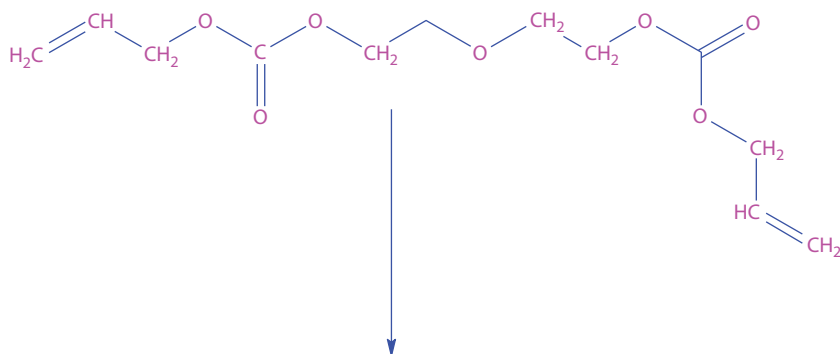
Thus, the applications of glass are many and expanding.

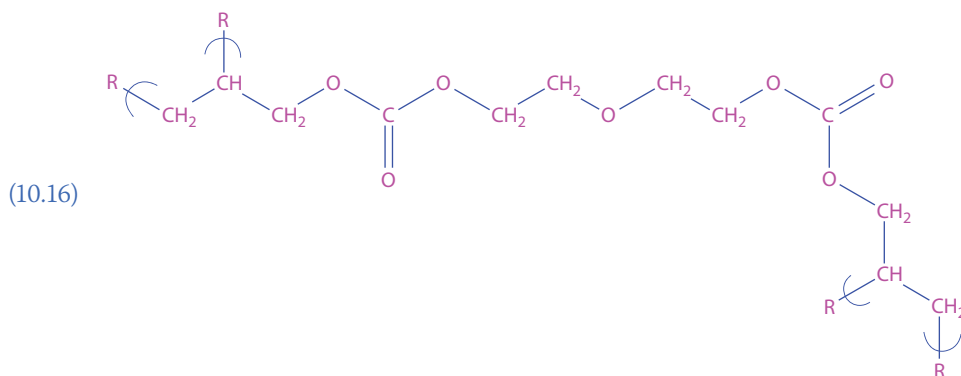
10.5.4 SEEING GLASS LENSES

By 1000 AD, reading stones became used. These were segments of a glass sphere that were used to magnify letters. The reading stones were placed directly on the letters. By 1350 AD, reading stones were hung with ribbons and strings near the eyes allowing the “wearer” to magnify objects within their “sight.” In 1730, a London optician, Edward Scarlett, developed rigid sidepieces that rested on the ears of the user. These were the first somewhat modern reading and seeing glasses. The first bifocals were developed by Benjamin Franklin by cutting two lenses in half and placing one above the other.

Before the 1960s, the lenses of glasses changed from “glass” to other materials generally known simply as “plastic lenses.” During this time safety glass lenses were made of polycarbonate. In comparison to crown glass, the polycarbonate and other “plastic” lenses were lighter and thinner, offered greater impact resistance, and were more flexible. For regular glass lenses, the “plastic” lenses referred to by the sales people at eye glasses outlets as simply “plastic” is CR-39. The “CR” stands for Columbia Resin and the 39 was the batch or formula made by the Columbia Laboratories in Ohio. CR-39 is made from allyl diglycol carbonate (or diethylene glycol bis(allyl carbonate)) monomer. On heating, the two vinyl groups open-up forming a cross-linked thermoset plastic that cannot be resoftened on heating. This is described in the following text where the CR-39 Monomer (10.15) is polymerized forming CR-39 Polymer (10.16). By comparison, polycarbonate is a linear plastic that is a thermoplastic that can be resoftened, and recycled, on addition of heat and pressure. The lenses are formed by melting polycarbonate pellets and injecting them into a mold. Lenses from CR-39 are made by casting the monomer into appropriate molds followed by polymerization creating the lens either as a finished product or further working the solid lens material creating the finished lens.

(10.15)





The CR-39 lenses are less scratch resistant than polycarbonate lenses and much less scratch resistant compared to glass. In the 1970s the 3M (Minnesota Mining and Manufacturing Company) company had a research group that was expert in coatings including lenses. One problem was the need, for some materials, to have them particularly free from dust to achieve mar-free coated surfaces. By the mid-1970s, they created a production facility that reduced airborne particles sufficiently to allow materials to be successfully coated. In 1979, 3M purchased the Armorlite Company and transferred their scratch-resistant coating technology to be used for the CR-39 lenses. American Optical introduced photolite photochromic lenses that change color with exposure to light in 1981. PPG, in 1983, discovered a new family of photochromics, the blue pyridobenzoxanines, and by 1984 formed a joint venture with Intercast-Europe to manufacture and sell photochromic sunglasses called Attiva sunglasses made from CR-39. Many other companies have contributed to the presence of today's plastic lenses. The story illustrates how companies apply their interests and strengths to achieve the products we have today.

Today, there are new so-called high index lenses, made from a variety of polymers that are thinner than CR-39 and polycarbonate lenses that can be purchased from a variety of outlets (Picture 10.9).



PICTURE 10.9 Glasses of many sorts, materials, and prices can be purchased at local store outlets.

10.6 SOL–GEL

In the sol–gel process, ceramic polymer precursors are formed in solution at ambient temperature; shaped by casting, film formation, or fiber drawing; and then consolidated to furnish dense glasses or polycrystalline ceramics. The most common sol–gel procedures involve alkoxides of silicon, boron, titanium, and aluminum. In alcohol–water solution, the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which subsequently form $-M-O-M-$ linkages. Branched polymer chains grow and interconnect forming a network that can span the entire solution volume. At this point, the gel point, the viscosity, and elastic modulus rapidly increase.

The gel is a viscoelastic material composed of interpenetrating liquid and solid phases. The network retards the escape of the liquid and prevents structural collapse. The shapes formed by casting, drawing of fibers, or film formation are locked in by the gel formation. Some gels are oriented by drawing or shearing. The gel is dried by evaporation forming a xerogel or by supercritical fluid extraction giving an aerogel. Consolidation to dense glasses or ceramics is carried out by thermal treatment and sintering.

Since both aerogels and xerogels have high surface areas and small pore diameters, they are used as ultrafiltration media, antireflective coatings, and catalysts supports. Final densification is carried out by viscous sintering.

The rate of silicate sol and gel formation is pH and water–alcohol sensitive as is the solubility of the amorphous silica that is formed. Silica networks are based on $(SiO_4)^{-4}$ tetrahedra modified by (O_3Si-O^-) , M^+ units and often with addition of boron oxide, aluminum oxide, titanium IV oxide, or zirconium IV oxide.

The nature of the reactants can be varied giving various silicate-like products. The following (10.17, 10.18) describes the formation of borosilicate glasses using the sol–gel approach:



The use of organically modified silicates (ceramers) gives a wide variety of products with a variety of structures and properties. Such ceramers have been used as adhesives for glass surfaces, protective coating for medieval stained glass, and scratch-resistant coatings for plastic eyeglass lenses. They have also been used in the reinforcement of plastics and elastomers, and their nanoscale pores allow their use as porous supports and as selective absorbents.

Sol–gel preparations of tetraethoxysilane can be spun into fibers once the appropriate viscosity has been achieved. These fibers are only slightly weaker than silica glass fibers.

Hybrid materials have been made by incorporating end-capped poly(tetramethylene oxide) blocks to tetramethoxysilane sol–gel glasses. These materials have high extensibility with interdispersed organic and inorganic regions.

10.6.1 AEROGELS

Aerogels are highly porous materials where the pore sizes are truly on a molecular level, less than 50 nm in diameter. This gives a material with the highest known internal surface area per unit weight. One ounce can have a surface area equal to 10 football fields, over 1000 m² in 1 g.

Porous materials can be either open-pored such as a common sponge or closed pored such as the bubble wrap packaging. Aerogels are open-pored materials such that unbonded material can move from one pore to another.

While in the gel state, the pre-aerogel has some flexibility, but as a solid, aerogels behave as a fragile glass. It may be very strong in comparison to its weight, but remember it is very light. Aerogels are more durable when under compression. Aerogels are best cut using a diamond coated saw similar to that used by rock cutters to slice rocks.

When handled, aerogel samples will initially appear to exhibit some flexibility but then burst into millions of pieces. For large arrays of atoms, such as solid metals and polymers below their glass transition temperature, energy can be absorbed through bond flexing or bending. For polymers between their glass transition and melting points, kinetic energy can also be absorbed through segmental movement. Silica aerogels, being an inorganic polymer in the glassy state at room temperature, is a brittle material. As force is applied, there is very little bond flexing, so that the applied kinetic energy results in the collapse of the network with the force of impact spread over a large part of the aerogel and over a time because of the time required to transfer this energy from one cell to another within the aerogel matrix. Because the aerogel is open-pored, gas contained within the solid is forced outward as collapse occurs. The frictional forces caused by the gas passing through a restricted opening are indirectly proportional to the square of the pore diameter. Because the pore sizes are so small, the rapidly moving gas also absorbs a lot of the energy. Thus, energy is absorbed by the aerogel through both collapse of the solid network structure and release of the gas within the aerogel.

Aerogels contain particles that are about 2–5 nm in diameter with large surface-to-volume ratios on the order of 10^9 m^{-1} and high specific surface areas approaching $1000 \text{ m}^2/\text{g}$. Such large surface-to-volume ratios make the surface particularly active and potential materials as catalysts, absorbents, and catalyst substrates.

The precise chemical makeup of the surface depends on the materials used to make the aerogel and method of processing. Typical aerogel sequences produce products whose surfaces are rich in hydroxyl groups. Because of the high surface area, $-\text{Si}-\text{OH}$ groups act as weak acids and are reactive in typical Lewis acid–base reactions. As noted before, aerogels have many hydrogen-bonding hydroxyls at their surface making aerogels extremely hygroscopic. Dry aerogel materials will increase their weight by 20% through uptake of moisture from the air. This absorption is reversible and appears to have little or no effect on the aerogel. Water is removed through heating to 100°C – 120°C .

While adsorption of water vapor has little effect on aerogels, contact with liquid water has devastating effects on aerogels. When water enters the nanometer-size pores, the surface tension of the water exerts capillary forces sufficient to fracture the silica backbone resulting in a collapse of the complex matrix structure. This tendency to be attacked by water is overcome through conversion of the surface polar $-\text{OH}$ groups to nonpolar $-\text{OR}$ groups. The “R” is typically a trimethylsilyl group though any aliphatic group would work. Conversion can be accomplished within the wet stage (pre-aerogel) or after the supercritical drying. These treatments result in an aerogel that is called “hydrophobic” aerogel, which is stable in water.

The pore size of aerogels varies. The International Union of Pure and Applied Chemistry classifies materials with pore sizes of less than 2 nm as “micropores,” 2–50 nm are called “mesopores,” and those greater than 50 nm in diameter are called “macropores.” While aerogels have some pores that fall within the micropore region, the majority of pores are in the mesopore region.

Most of the aerogels produced today are described as being transparent. While it might be assumed that, since aerogels are made of the same material as window glass and quartz, SiO_2 , they would be transparent, this is not necessarily the case. Transparency requires a number of factors. Thus, the so-called smokey and white quartz are colored because of the presence of impurities. Mixtures of amorphous and crystalline silicon dioxide can be made that are not transparent. The size and distribution of reflecting and refractive sites are important factors in determining if a material is transparent with the theme of “sameness” contributing to making a material transparent.

The majority of light we see is scattered light, that is, light that reaches our eyes in an indirect manner. The scattering phenomenon is what gives us blue skies, white to gray clouds, and poor visibility in fog. This scattering is not simply reflecting but results from the interaction of light with an inhomogeneous site. Light scattering photometry is used to determine the size of polymers. Scattering is most effective when the scattering particle size is about that of the wavelength of the light. For visible light, this occurs with scattering sites that are about 400–700 nm. Scattering centers that are much less than the incoming light wavelength are much less effective at scattering the light. Since the particle sizes in an aerogel are much smaller, the individual sites are ineffective scattering sites. Similar to classical polymer chains, where the entire chain or segments of the entire chain act as a scattering site, clusters of individual sites within the aerogel act as scattering sites. Most of these scattering sites are again smaller than the wavelength of visible

light, but some are within the range to scatter visible light so that a soft reflected light results. The different-sized scattering sites and variable wavelengths present in light cause a reddening of the transmitted light (red light has a longer wavelength and is scattered less by small clusters present in the aerogel) resulting in the blue appearance of the reflected light from the aerogel.

The good visible light transmission and good insulating power make aerogel materials of interest in window manufacturing. The visible transmission spectra of light shows little absorption in the range of about 300–2700 nm giving aerogels a good visible light “window” making aerogels attractive for daylighting applications. Aerogels provide about 40-fold more insulation than does fiberglass insulation. While such aerogels may eventually be used as the entire window component, currently they may act as the material sandwiched between two panes of clear plastic or glass. “*Thermoglass*” is generally simply glass sheets that are separated by a vacuum. The seals on such thermoglass often spring small leaks causing greater diminished insulation properties. Aerogel inner cores will not suffer from this problem. Currently, about 40%–50% of a house’s heating bill literally goes out the window because of lost heat or cold through windows. A single 1 in. thick glass pane of aerogel offers the insulation equivalent to over 30 windowpanes of R-20 insulation rated glass.

Another commercial area that is being considered is the use of aerogels as nanocomposite materials. Approaches are varied. In one approach, material is added to the silica sol before gelation. The material can be inorganic, organic, polymeric, bulk fibers, woven cloths, etc. The additional material must be able to withstand the subsequent processing steps including carbon dioxide drying. The added material must be present in a somewhat homogeneous manner throughout the system. Gentle agitation appears to be sufficient to give a product with decent homogeneity. Aerogels may be good materials for optical sensors. They have good visible transparency, high surface area, good temperature and chemical stabilities, and facile transport of gases through their pores.

10.7 SILICON DIOXIDE (CRYSTALLINE FORMS): QUARTZ FORMS

Just as silicon dioxide forms the basis of glass, so also does it form the basis of many of the rocks, grains of sand, and dirt particles that compose Earth’s crust (Picture 10.10). Most rocks are inorganic polymers, but here we will deal with only a few of these containing significant amounts of silicon.



PICTURE 10.10 Purple, pink, white, and clear natural quartz and quartz containers that hold samples for analytical analyses.

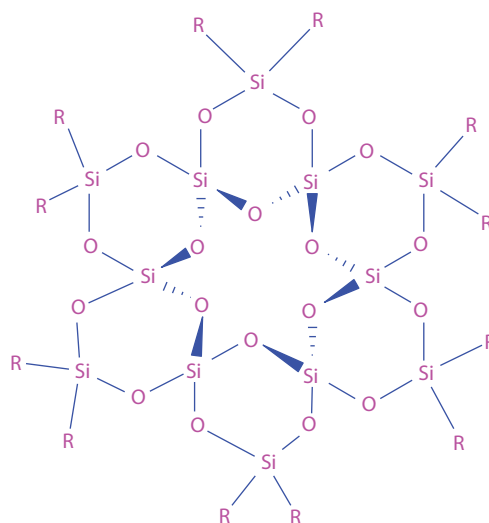


FIGURE 10.4 Structure of crystalline SiO_2 tetrahedra found in quartz.

Silicon oxide crystallizes in mainly three forms—quartz, tridymite, and cristobalite. After the feldspars, quartz is the most abundant material in Earth's crust, being a major component of igneous rocks and one of the most common sedimentary materials, in the form of sandstone and sand. Quartz can occur as large (several pounds) single crystals, but normally is present as granular materials. The structure of quartz (Figure 10.4) is a 3D network of six-membered Si–O rings (three SiO_4 tetrahedra) connected such that every six rings encloses a 12-membered Si–O (six SiO_4 tetrahedra) ring.

Quartz is found in several forms in all three major kinds of rocks—igneous, metamorphic, and sedimentary. It is one of the hardest minerals known. Geologists often divide quartz into two main groupings—coarse crystalline and cryptocrystalline quartz. Coarse crystalline quartz includes six-sided quartz crystals and massive granular clumps. Some colored varieties of coarse crystalline quartz crystals, amethyst and citrine, are cut into gem stones. Others include pink (rose), purple, and milky quartz, but most coarse crystalline quartz is colorless and transparent. Sandstone is a ready example of granular quartz. Color is a result of the presence of small amounts of metal cations such as calcium, iron, magnesium, and aluminum.

Cryptocrystalline forms contain microscopic quartz crystals and include the chalcedony grouping of rocks such as chert, agate, jasper, and flint.

Quartz exhibits an important property that allows the “[piezoelectric effect](#).” When pressure is applied to a slice of quartz, it develops a net positive charge on one side of the quartz slice and a negative charge on the other side. This phenomenon is the piezoelectric generation of a voltage difference across the two sides of the quartz crystal. Furthermore, the same effect is found when pressure is applied not mechanically, but through application of an alternating electrical field with only certain frequencies allowed to pass through the crystal. The frequencies allowed to pass vary with the crystal shape and thickness. Such crystals are used in radios, televisions, and radar. This effect also forms the basis for quartz watches and clocks. Voltage applied to a quartz crystal causes the crystal to expand and contract at a set rate, producing vibrations. The vibrations are then translated into a uniform measure of time.

While quartz crystals are suitable for the production of optical lenses, most lenses are manufactured from synthetically produced quartz due to the scarcity of good-grade large quartz crystals.

The feldspars are the most abundant minerals in Earth's crust, accounting for about 60% of all igneous rocks. They are derivatives of silica, where about one-half or one-quarter of the silicon atoms have been replaced by aluminum. Feldspar is used in the manufacture of certain types of glass and pottery. Some feldspar crystals—such as moonstone (white perthite), Amazon stone (green microcline), and multicolored labradorite—are used as gem stones and in architectural decorations. Some feldspar is used as a coating and filler in the production of paper.

“Granite” is a hard crystalline rock chiefly composed of quartz and feldspar. It is used in building bridges and building where great strength is needed. It is also employed in the construction of monuments and gravestones since it can be polished giving a lasting luster and because of its ability to withstand wear by the natural elements.

Sand is loose grains of minerals or rocks, larger than silt but smaller than gravel. Soil contains mineral (often in the form of small sand granules) and organic matter.

“Micas” are also composed of silicon–oxygen tetrahedra. The anionic charge on the silicate sheet is the result of the replacement of silicon by aluminum. Cations such as potassium are interspaced between these negatively charged sheets. Some micas are used in construction and electrical engineering applications. Synthetic mica is manufactured on a large scale for industrial consumption in coatings, such as fillers. Micas are one of the many layered silicon-oxygen-intense materials found in nature.

10.8 SILICON DIOXIDE IN ELECTRONIC CHIPS

Silicon dioxide plays a critical role in the electronics industry. The silicon used to produce silicon chips is derived from silicon dioxide (10.19). Semi-pure silicon dioxide (to about 99%) is prepared from the reaction of silicon dioxide with coke (a poor grade of graphite) using high temperature and an electronic arc.



Even so, this level of purity falls far short of the purity needed to produce the chips used in computers. The purity required is about 99.9999996 or a level of impurity of about one part in a billion. This is achieved through multistep processes. One of these requires the silicon to be heated with HCl at high temperatures forming the desirable volatile trichlorosilane (10.20). The vapor is condensed and then purified using distillation and absorption columns. The trichlorosilane is reacted with hydrogen gas at about 1200°C depositing polycrystalline chip-grade silicon (10.21). The other product of this reaction is HCl, which can be again used to create more trichlorosilane, thus eliminating the production of unwanted by-products.



Silicon dioxide is also used to insulate regions of the integrated circuit. Here silicon dioxide is grown on the silicon surface by heating the surface to about 1000°C in the presence of oxygen (10.22).



An alternate approach employs heating gaseous tetraethoxysilane to form layers of silicon dioxide (10.23).



10.9 ASBESTOS

Asbestos has been known and used for over 2000 years. Egyptians used asbestos cloth to prepare bodies for burial. The Romans called it *aminatus* and used it as a cremation cloth and for lamp wicks. Marco Polo described its use in the preparation of fire-resistant textiles in the thirteenth century. Asbestos is not a single mineral but rather a grouping of materials that give soft, threadlike fibers. These materials will serve as an example of 2D sheet polymers containing 2D silicate $(\text{Si}_4\text{O}_{10})^{4-}$ anions bound on either or both sides by a layer of aluminum

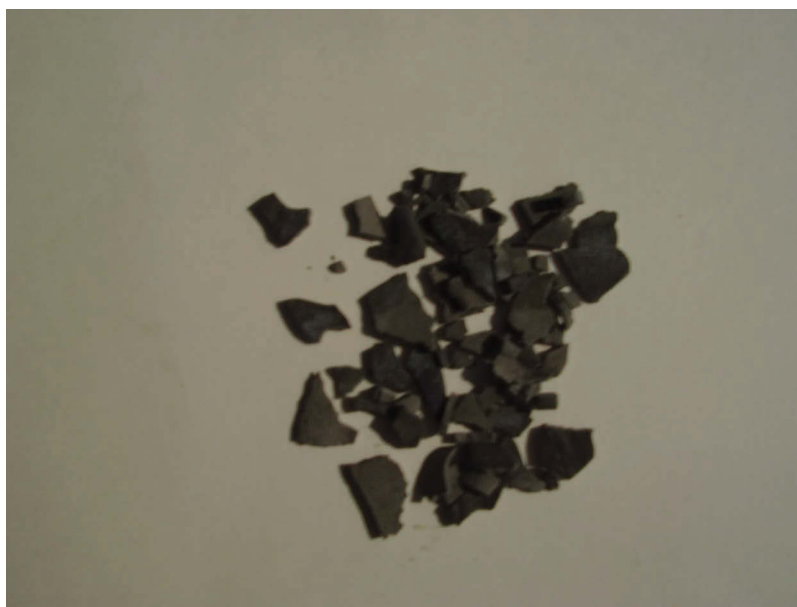
hydroxide ($\text{Al}(\text{OH})_3$; gibbsite) or magnesium hydroxide ($\text{Mg}(\text{OH})_2$; brucite). Aluminum and magnesium are present as positively charged ions. These cations can also contain varying amounts of water molecules associated with them as hydrates. The spacing between silicate layers varies with the nature of the cation and amount of its hydration.

Due to its fibrous nature and ability to resist elevated temperatures (compared with most organic-based fabrics), it is used to make fabrics for the production of fire-resistant fabric including laboratory glove wear. Shorter fibers were used in electrical insulation, building insulation, and automotive brake linings. Though asbestos has been known for thousands of years, it has only recently become known that asbestos can be dangerous. For instance, asbestos miners and manufacturing personnel who worked with it for 20 years or longer are 10 times more likely to contract asbestosis. Families of these workers and those living near the mines also have a greater than average chance of getting asbestosis. Asbestosis is a disease that blocks the lungs with thick fibrous tissue, causing shortness of breath, and swollen fingers and toes. Bronchogenic cancer (cancer of the bronchial tubes) is prevalent among asbestos worker who also smoke. Asbestos also causes mesothelioma, a fatal cancer of the lining of the abdomen or chest. These diseases may lay dormant for many years after exposure. It is believed that these diseases are caused by asbestos particles (whether asbestos or other sharp particles) about 5–20 μm in length corresponding to the approximate sizes of the mucous openings in the lungs. Thus, they become caught in the mucous openings. Because they are sharp, they cut the lining when people cough. Scar tissue and the repeated healing process cause scar tissue buildup and the opportunity for cancerous mutations to begin.

10.10 FLY ASH AND ALUMINOSILICATES

Aluminosilicates or aluminum silicates include industrial waste materials such as fly ash from the burning of coal and ground-granulated blast furnace slag and natural materials such as metakaolin, kaolin, microsilica, and volcanic ash. All are inorganic polymers derived from aluminum oxide and silicon oxide.

Fly ash is one residue created from the combustion of coal (Picture 10.11). Because there are different sources of coal, fly ash has a variable composition. Table 10.7 contains the general chemical composition as a function of the three major varieties of coal.



PICTURE 10.11 Aluminum silicates derived from the burning of coal.

TABLE 10.7 Percentage Average Chemical Composition of Fly Ash Derived from Different Coals

Composition	Bituminous	Subbituminous	Lignite
SiO ₂	20–60	40–60	15–45
Al ₂ O ₃	5–35	20–30	20–25
FeO, Fe ₂ O ₃	10–40	5–10	5–15
CaO	1–12	5–30	15–40

Fly ash consists of a variable mixture of somewhat spherical glasses ranging in size from 0.5 to 100 μm in diameter. It also contains minute amounts of many other elements including arsenic, beryllium, boron, barium, copper, cadmium, chromium, thallium, vanadium, zinc, strontium, lead, and nickel. Fly ash is further divided by ASTM C618 standards into two general groupings, Class F and Class C. Class F typically comes from the combustion of older anthracite and bituminous coal that contains less than 10% lime (CaO). Pozzolanic materials combine with calcium hydroxide forming a cement-like material. Class F fly ash is pozzolanic with the glassy silica and alumina requiring a cementing agent such as Portland cement and water to produce a cement. Class C fly ash generally comes from younger lignite and subbituminous coal. Along with being pozzolanic, it is more self-cementing in comparison to Class F fly ash containing more lime, alkali, and sulfates.

Fly ash was used to be simply land fill but recycling is increasing. Coal burning power plants produce about 80 million tons of fly ash yearly in the United States. About 30 million tons are currently recycled. Recycling of fly ash also reduces the need to quarry and the energy related to preparing concretes such as Portland cement. Fly ash is used with Portland cement allowing the amount of Portland cement to be reduced by up to 30% by mass. The resulting concrete is often greater in strength compared to employing only Portland cement. The use of fly ash to replace Portland cement is considered green friendly since the production of one ton of Portland cement produces about one ton of carbon dioxide in comparison to zero carbon dioxide for fly ash.

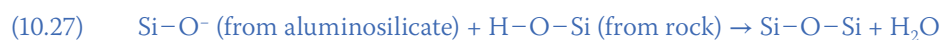
Unlike soils, fly ash is more uniform in particle size so its addition to soil gives the mixture some interesting properties. Fly ash is used in the production of flowable fill or controlled low strength material. It is used as a self-leveling, self-compacting backfill.

Asphalt concrete is a composite of asphalt and a mineral aggregate. Fly ash is used to fill voids between larger aggregates. Fly ash-containing asphalt concrete is stiffer resisting rutting.

Fly ash is a source of what is referred to as geopolymers. This term covers a group of inorganic synthetic aluminosilicate materials. Other major sources of geopolymer are volcanic materials and the slag from metal smelting. Aluminosilicates are actually a mixture where much of the material exists as fused ring clusters as shown in Figure 10.5.

Fly ash and aluminosilicate use is considered to be environmentally conscious in that they are otherwise disposed in landfills and can substitute for materials with a large CO₂ footprint, but themselves they have no CO₂ footprint.

Each of these structures contain ionic oxygen “fingers” that can react with silicon oxide and vacant silicon sites on the sand and rocks of the concrete forming chemical bonds between the aluminosilicate concrete (10.24 through 10.27). Thus, aluminosilicates are being used as additives to Portland cement and as a building material themselves.



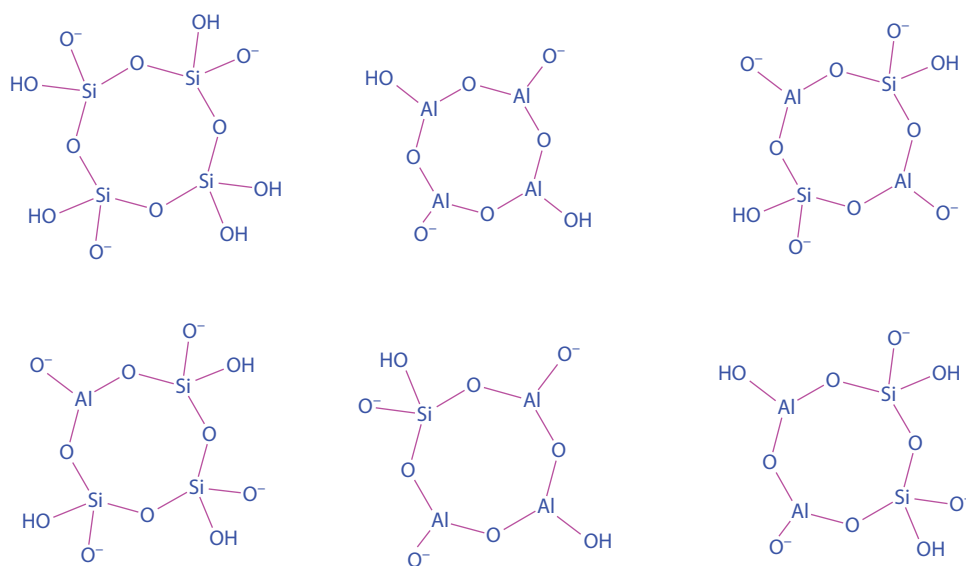


FIGURE 10.5 Examples of aluminosilicate rings including those containing only silicone (top left) and only aluminum (top middle).

These bonds can also be formed through the calcium oxide portions of the concrete ((10.28) and (10.29)):



These inorganic polymers have a chemical composition similar to mica and zeolites but they are amorphous rather than crystalline.

The aluminosilicate geopolymers are generally formed from reaction of an aluminosilicate powder with an alkaline silicate solution or other activator.

Aluminum silicates serve as the basis for a number of specialty glasses including what became known as CorningWare. CorningWare was accidentally discovered by Donald Stookey in 1952. He heated some FotoForm glass mistakenly to 900°C rather than the intended temperature of 600°C. FotoForm glass is a photosensitive aluminum silicate-based material. When he opened the oven he expected to find a molten mess but rather found that the material crystallized forming a strong shatterproof glass. Corning improved the material and sold the material as Pyroceram. The material had good thermal and physical stability and was employed to make a variety of products including nose cones of radar-guided missiles and the well-known line of kitchenware known as CorningWare.

10.11 POLYMERIC CARBON: DIAMOND

Just as carbon serves as the basic building element for organic materials, so it also forms a building block in the world of inorganic materials. Elemental carbon exists in many different forms including the two longest known—diamond and graphite. Graphite is the more stable allotrope of carbon, with graphite readily formed from heating diamonds.

Natural diamonds (Figure 10.6a) are believed to have been formed millions of years ago when concentrations of pure carbon were subjected by Earth's mantle to great pressures and heat. They are the hardest known natural material.

The majority of diamonds (nongem) are now man-made. Most of the synthetic diamonds are no larger than a grain of common sand. The major use of synthetic diamonds is as industrial shaping and cutting agents to cut, grind, and bore (drill). By 1970, General Electric was manufacturing diamonds of gem quality and size through compressing pure carbon under extreme

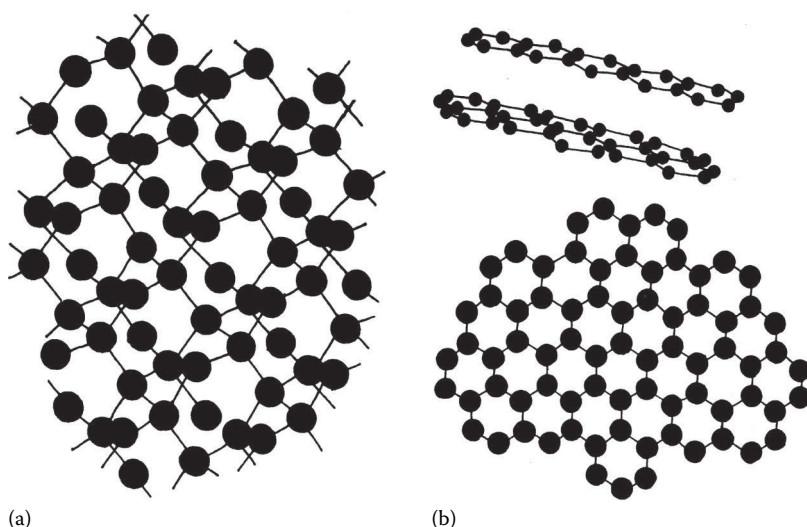
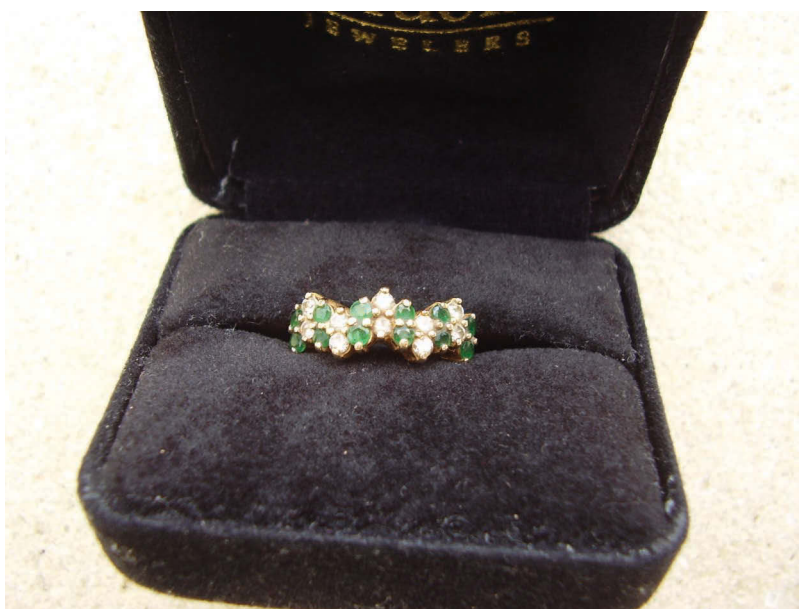


FIGURE 10.6 (a) Representation of diamond where each carbon is at the center of a tetrahedron composed of four other carbon atoms. (b) Representations of graphite emphasizing the layered (top) and sheet (bottom) nature of graphite.

pressure and heat. It was found that addition of small amounts of boron to diamonds causes them to become semiconductors. Today, such doped diamonds are used to make transistors.

Today, diamond-making technology is able to make jewelry quality lab diamonds that are practically identical to natural diamonds yet that cost about 50% less. Synthetic diamonds require a small diamond to use as a “seed” set in a carbon environment that allows the carbons to be added carbon atom by carbon atom over 6–12 weeks.

While diamonds can be cut, shaping is done by trained gem cutters striking the rough diamond on one of its cleavage planes. These cleavage plates are called faces and represent sites of preferential cleavage and reflection of light. This balance between strength and flexibility, crystalline and amorphous regions is demonstrated to one extreme by diamonds that are very crystalline resulting in a strong, inflexible, and brittle material. (Picture 10.12; Emerald is a variety of beryl,



PICTURE 10.12 My wife’s diamond and emerald engagement ring.

$\text{Be}_2\text{Al}_2(\text{SiO}_3)_6$, with the green color caused by trace amounts of chromium and sometimes vanadium. It is another example of the silicate-based polymers.)

10.12 POLYMERIC CARBON: GRAPHITE

While diamond is the hardest naturally occurring material, the most common form of crystalline carbon is the much softer and flexible graphite. Graphite occurs as sheets of hexagonally fused benzene rings (Figure 10.6b) or “hexachicken wire.” The bonds holding the fused hexagons together are traditional covalent bonds. The bonds holding the sheets together are weaker than the bonding within the sheets consisting of a weak overlapping of pi-electron orbitals. Thus, graphite exhibits many properties that are dependent on the angle at which they are measured. They show some strength when measured along the sheet, but very little strength if the layers are allowed to slide past one another. This sliding allows the graphite its flexibility, much like the bending of bundles of proteins sliding past one another allowing our hair flexibility. The fused hexagons are situated such that the atoms in each layer lie opposite to the centers of the six-membered rings in the next layer. This arrangement further weakens the overlapping of the pi electrons between layers such that the magnitude of layer-to-layer attraction is on the order of ordinary secondary van der Waals forces. The “slipperiness” of the layers accounts for graphite’s ability to be a good lubricant.

The variance of property with angle of applied force, light, magnetism, etc., is called anisotropic behavior. Calcite is anisotropic in its crystal structure, resulting in a dependency of its interaction with light with the angle of incidence of the light.

As with diamond, graphite’s discovery and initial usage is lost in antiquity. It was long confused with other minerals such as molybdenite (MoS_2). At one time it was known as plumbago (like lead), crayon noir, silver lead, black lead, and *carbo mineralis*. Werner in 1789 first named it *graphit*, meaning (in Greek) “to write.”

The Acheson process for graphite production begins by heating a mixture of charcoal, or coke, and sand. The silica is believed to be reduced to silicon that combines with carbon forming silicon carbide, which subsequently dissociates into carbon and silicon. The silicon vaporizes and the carbon condenses forming graphite. Graphite is also produced using other techniques.

Today, graphite is mixed with clay to form the “lead” in pencils (Picture 10.13). Graphite conducts electricity and is not easily burned so many industrial electrical contact points (electrodes)



PICTURE 10.13 Collection of “graphite” containing pencils.

are made of graphite. Graphite is a good conductor of heat and is chemically inert, even at high temperatures. Thus, many crucibles for melting metals are graphite-lined. Graphite has good stability to even strong acids; thus it is employed to coat acid tanks. It is also effective at slowing down neutrons, and thus composite bricks and rods (often called carbon rods) are used in some nuclear generators to regulate the progress of the nuclear reaction. Its slipperiness allows its use as a lubricant for clocks, door locks, and handheld tools. Graphite is also the major starting material for the synthesis of synthetic diamonds. Graphite is sometimes used as a component of industrial coatings. Dry cells and some types of alkali storage batteries also employ graphite. Graphite fibers are used for the reinforcement of certain composites.

10.13 INTERNAL CYCLIZATION: CARBON FIBERS AND RELATED MATERIALS

There are a number of important polymers that are formed through internal cyclization. In almost all cases, these are five- and six-membered rings with the vast majority being six-membered. The tendency to form six-membered rings is related to a statistical feature. In studying the most probable distances from the beginning point using random statistics for units with a bond angle of about 109.5° (for a tetrahedral), the most probable distance for a chain of six units long is back at the starting point. The number of units required before the most probable distance is the starting point is dependent upon the bond angle and is called the *Kuhn element*. As noted before, the Kuhn element for connected methylenes is six. The Kuhn element for sp^2 geometry is not six, but in this case, the driving force is the formation of six-membered rings with three alternating pi bonds—that is, the formation of the aromatic structure.

Often these internal cyclizations are incomplete giving products with mixed moieties. Even so, such internal cyclization is the source of a number of interesting and important polymers. A number of ladderlike structures have been synthesized from the internal cyclization of polymers. The following are several examples that illustrate this. The most important commercial products are those utilized to form the so-called carbon fibers.

Carbon fibers, and associated composite materials, are the result of internal cyclization. Polyacrylonitrile (PAN), when heated, undergoes internal addition forming a condensed polycyclic material called “black orlon.” Further heating to about 1000°C removes the hydrogen atoms and most of the nitrogens giving a polyaromatic structure containing about 95% carbon (Figure 10.7). Further heating to about 2800°C gives a product with almost 99% carbon.

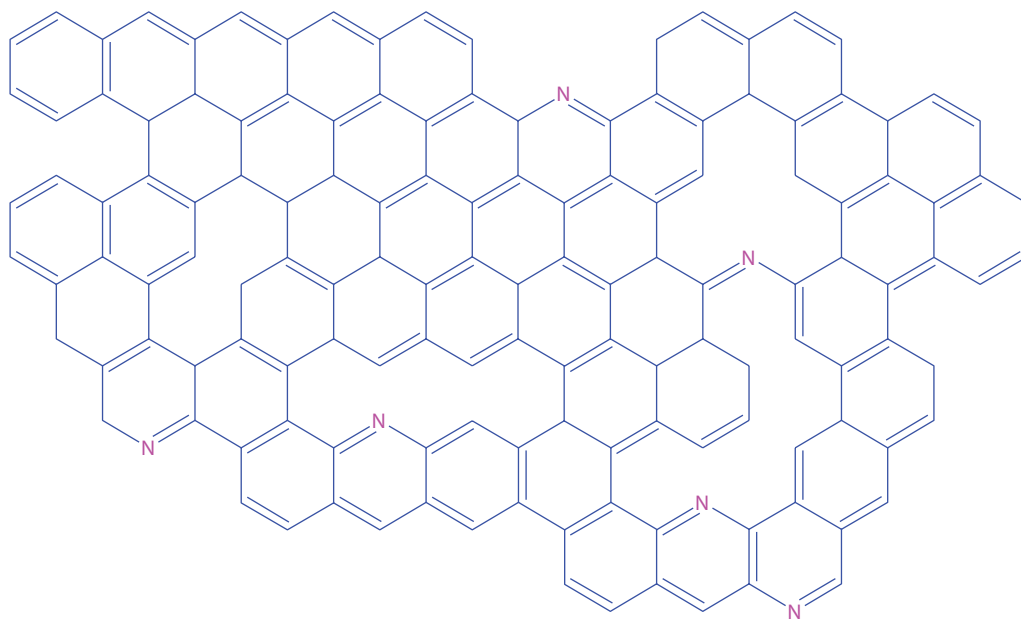


FIGURE 10.7 Idealized structure of “black orlon.”

These products can be forced through tiny holes to form tiny fiber-like materials, fibrals, which are combined to give fibrous-like materials that can finally be woven together to give fabrics. The fibrals, fibers, and fabrics act as the fibrous portion of many high-strength composite materials. These fibers are lightweight, very strong, and chemically inert and can form semiconductor and conductor materials.

The carbon fibers utilized in the construction of the new Airbus A350, Boeing 787 Dreamliner, and automotive (planned or real) exteriors and interiors are made from the PAN, which is extruded into fibers and carbonized in an oven. The fiber is woven into the desired part and then infused with epoxy or other resin creating the carbon fiber part. While there are many advantageous to such carbon fiber parts such as lack of rusting, high strength, energy dampening, and decreased weight, the fiber parts are relatively expensive with a cost of about \$30/kg compared with steel at about \$7/kg. This may add up to \$5000 to the cost of a car. Currently, most polymer composite automobiles are using fiberglass composites but the greater use of carbon fibers is beginning. BMW is using carbon fibers on the battery-powered i3 and the hybrid i8. Daimler is producing passenger cages and doors of carbon fiber for the Smart Forvision. Alternatives to PAN as to the carbon source are also being considered including polyethylene and lignin.

Diene polymers undergo cyclization in the presence of cationic initiators such as sulfuric acid. 1,2- and 3,4-diene polymers undergo this cyclization forming extensive fused ring groupings.

The polymerization of butadiene using certain catalytic systems such as butyl lithium and tetramethylenethylene diamine gives poly(1,2-polybutadiene). The polybutadiene, in turn, can undergo internal cyclization via cationic reactions forming a sort of linear saturated polycyclohexane. Further heating, resulting in dehydrogenation, with chloranil gives a fused ring product similar to that of carbon fibers when heated to about 1500°C (Figure 10.7). This material is sold under the trade name Pluton by 3M. This sequence is described in Figure 10.8. While the final product is insoluble and infusible, pre-spinning is done on the soluble saturated intermediate.

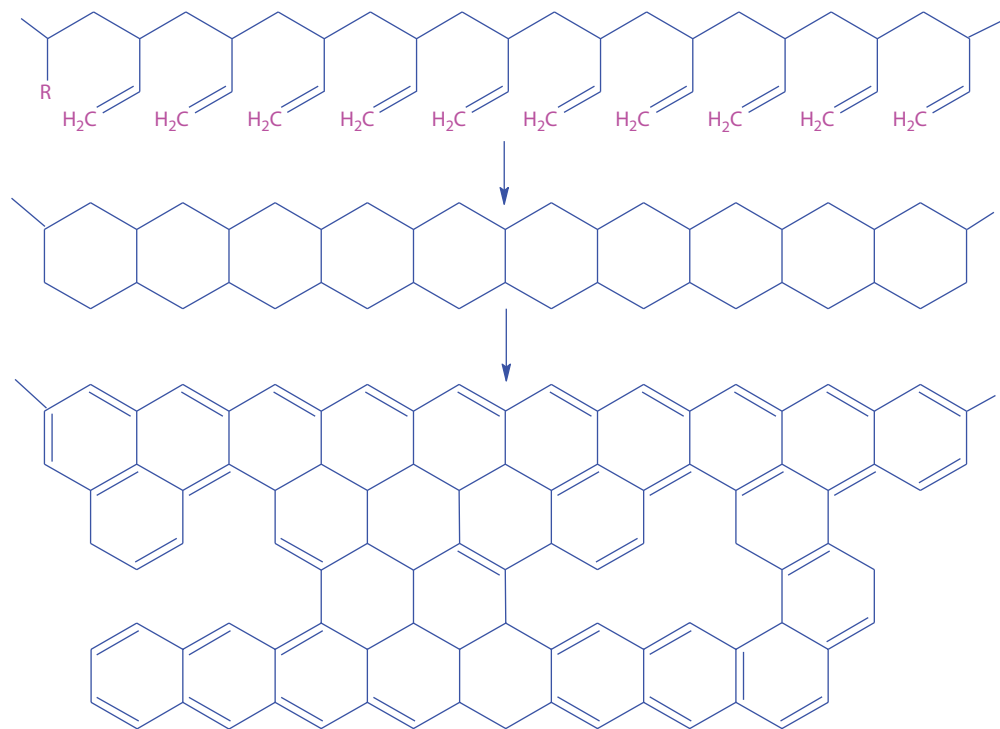


FIGURE 10.8 Idealized structures for the synthesis of carbon-like materials from poly(1,2-butadiene).

10.14 CARBON NANOTUBES

10.14.1 GENERAL

There are several materials that form so-called nanotubes including boron–nitrogen compounds. Here we will focus on nanotubes derived from carbon. Carbon nanotubes (CNTs) have probably been made in small amounts since the first fires reduced trees and organic material to ashes. It has been found that certain ancient steel products may have possessed CNTs derived from the exposure of the processed steel to carbon sources. Thus, the Damascus steel used in making very strong weapons is believed to have profited from the presence of CNTs. It was not until recently, as part of the so-called nano-revolution, that we first recognized the existence of these nanotubes. In 1952, Radushkevich and Lukyanovich published pictures of tubes of carbon. This discovery was largely unnoticed. Others contributed to the early history of carbon in the form of tubes. In 1991, Sumio Iijima of NEC Fundamental Research Laboratory in Japan first observed CNTs as by-products of the arc-discharge synthesis of fullerenes, and it is often accepted that this observation prompted the current activities with CNTs.

CNTs are carbon allotropes that have attracted much attention. They have a diameter of about 1/50,000 that of a human hair. Some have suggested that CNTs will be one of the most important twenty-first-century materials because of the exceptional properties and ready abundance of the feedstock, carbon. CNTs are generally classified into two groups. Multiwalled carbon nanotubes (MWCNTs) are generally comprised of 2–30 concentric graphitic layers with diameters ranging from 10 to 50 nm with lengths that can exceed 10 μm . Single-walled carbon nanotubes (SWCNTs) have diameters ranging from 1.0 to 1.4 nm with lengths that can reach several micrometers.

An ideal CNT can be envisioned as a single sheet of fused hexagonal rings, that is, graphite, which has been rolled up forming a seamless cylinder with each end “capped” with half of a fullerene molecule. SWCNT can be thought of as the fundamental cylindrical structure, with MWCNTs simply being concentric tubes. They can also be conceived of as being the fundamental building block of ordered arrays of SWCNTs called ropes.

10.14.2 STRUCTURES

CNTs are composed of carbon sp^2 -bonded structures, similar to those of graphite. These bonds are stronger than the sp^3 bonds resulting in the strength of the CNTs. Unlike 2D sheets of graphite, the CNTs align themselves into ropelike structures. Because of bonding similarity to graphite, these materials are often referred to as graphene.

Geometrically, CNTs can be described in terms of a 2D graphene (graphite) sheet. A chiral vector is defined on the hexagonal lattice as

$$(10.30) \quad C_h = n\mathbf{x} + m\mathbf{y}$$

where

\mathbf{x} and \mathbf{y} are unit vectors

n and m are integers, also tube indices

The chiral angle is measured relative to the direction defined by $n\mathbf{x}$.

When the graphene sheet is rolled up forming a nanotube, the two ends of the chiral vector meet one another. The chiral vector thus forms the circumference of the CNTs circular cross section. Different values of n and m give different nanotube structures with different diameters (Figure 10.9).

There are three general types of CNT structure (Figure 10.10). The zigzag nanotubes correspond to $(n,0)$ or $(0,m)$ and have a chiral angle of 0° . The carbon–carbon position is parallel to the tube axis. Armchair nanotubes have (n,n) with a chiral angle of 30° . The carbon–carbon positions are perpendicular to the tube axis. Chiral nanotubes have general (n,m) values and a chiral angle of between 0° and 30° , and as the name implies, they are chiral.

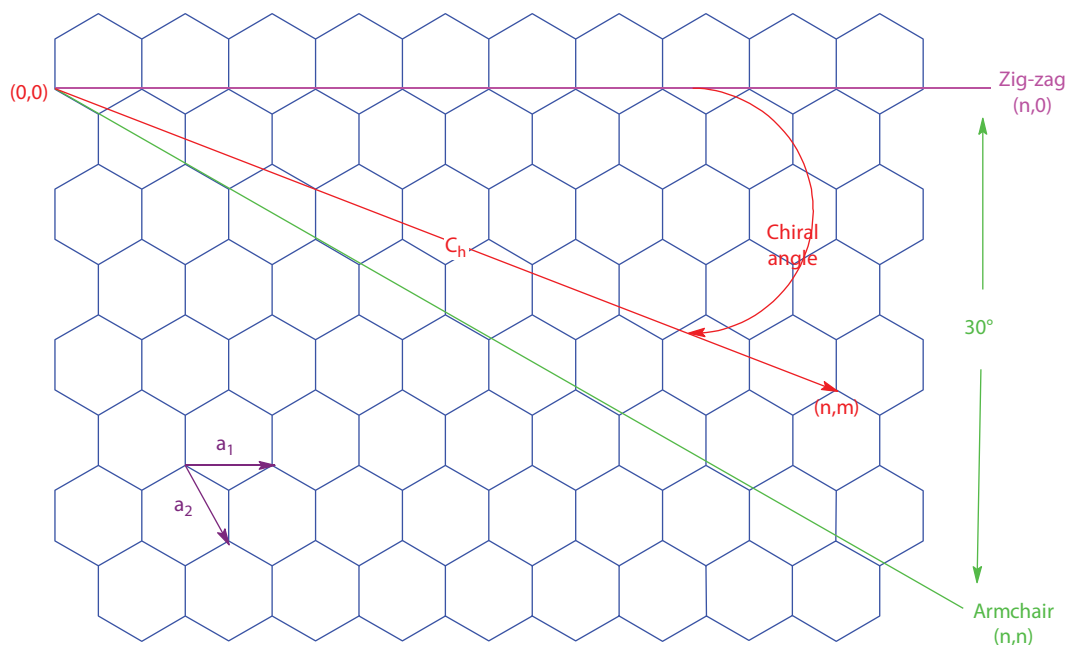


FIGURE 10.9 Graphite sheet representations showing the θ or chiral angle. For a chiral angle of 0° , the structure is a zigzag, for 30° it is an armchair, and in between it is helical. The figure is drawn with a 30° angle between the zigzag and armchair.

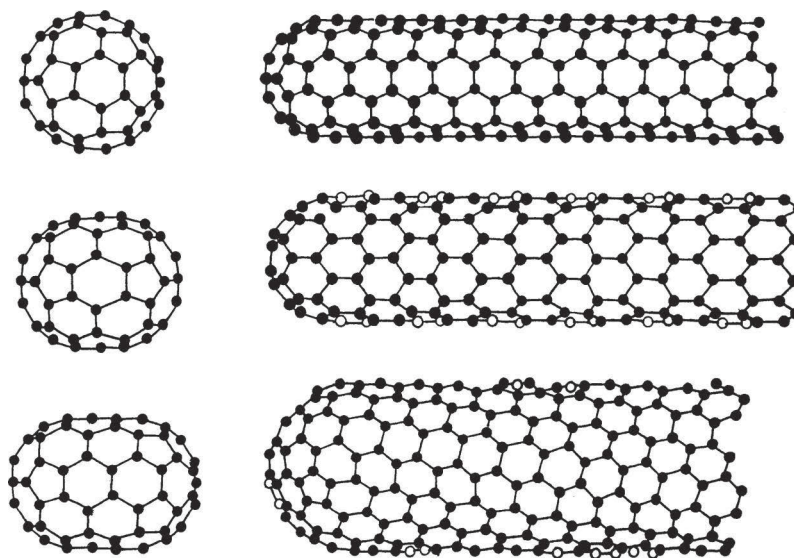


FIGURE 10.10 On the left side are representations of C_{60} (top), C_{70} (middle), and C_{80} (bottom) fullerene structures and on the right representations of the three major structural forms of carbon nanotubes: armchair (top), zigzag (middle), and helical (bottom).

In real life, nothing is perfect. As is the case with CNTs, the defects are mainly inclusion of wrong-membered rings. Pentagonal defects, that is, the replacement of a hexagonal with a five-membered ring, results in a positive curvature causing the tube to curve inward like a horseshoe. The closure of an open cylindrical surface necessarily involves topological defects—often formation of pentagons. Heptagonal defects result in a negative curvature with the lattice looking expanded around the defect.

The tendency to include pentagonal units can be seen by comparing the presence of pentagonal units in fullerene structures. The C_{60} structure contains 12 pentagons and 20 hexagons.

TABLE 10.8 Comparison between Selected Properties of Single-Walled Carbon Nanotubes and Competitive Materials/Techniques

Property	Single-Walled Carbon Nanotubes	Comparison
Size	0.6–1.8 nm in diameter	Electron beam lithography can create lines 50 nm wide and a few nm thick.
Density	1.33–1.40 g/cc	Aluminum has a density of 2.7 g/cc and titanium has a density of 4.5 g/cc.
Tensile strength	ca 45 billion Pascals	High-strength steel alloys break at about 2 billion Pascals.
Resilience	Can be bent at large angles and re-straightened without damage	Metals and carbon fibers fracture at grain boundaries.
Current carrying capacity	Estimated at 1 billion A/cc	Copper wires burn out at about 1 million A/cc.
Heat transmission	Predicted to be as high as 6000 W/m · K	Diamond transmits 3320 W/m · K.
Field emission	Can activate phosphors at 1–3 V if electrodes are spaced 1 μ m apart.	Molybdenum tips require fields of 50–100 V/ μ m and have limited lifetimes.
Temperature stability	Stable up to 2800°C in vacuum, 750°C in air	Metal wires in microchips melt at 600°C–1000°C.

The larger the fullerene, the smaller the ratio of pentagons to hexagons. This is consistent with the use of pentagons to “cause” sharper bends and greater curvature in comparison to hexagons. Interestingly, fullerene C_{60} is one of the most strained molecules known but it exhibits good kinetic stability. It begins to decompose at about 750°C. There are a number of higher-numbered (carbon number) fullerenes including C_{70} , C_{76} , C_{78} (two geometric isomers), C_{80} ,.... Fullerenes can act as a source of the CNTs with the different-sized fullerenes producing different nanotubes. The three general structures of nanotubes can be produced using different fullerenes with C_{60} giving armchair nanotubes, C_{70} giving zigzag structures, and C_{80} giving helical forms of nanotubes. Figure 10.10 contains representations of these three fullerenes.

This difference in structure also influences the electrical conductivity with the armchair form being conductive or metallike in its conductivity and most of the other forms act as semiconductors.

One of the major reasons for the intense interest in CNT is their extreme and varied properties. CNTs are among the strongest and stiffest materials known. Tensile strengths to about 65 gigapascals (GPa) have been found. This translates to a cable of 1 mm² cross section capable of holding about 3200 tons. A general density of CNTs is about 1.4 g/cc. Its specific strength is over 300 times as great as steel. Under stress, tubes can undergo permanent deformation, plastic deformation. Interestingly, because the tubes are hollow, they are not nearly as strong buckling under compression, torsion, and bending stress. Nanotubes conduct and transport along the lengthwise direction resulting in them often being referred to as being 1D.

Table 10.8 contains a comparison between SWCNTs and competitive materials/techniques. Another reason for the intense interest is that CNTs are produced from readily available inexpensive materials; they are being considered for use as both bulk materials, such as in composites and clothing, and as components in computers, electrical devices, etc. The following is a discussion of some of the application areas for CNTs.

10.14.3 PROPERTIES

10.14.3.1 ELECTRICAL

Nanotubes can be metallic or semiconducting, depending on their diameters and helical arrangement. Armchair ($n = m$) tubes are metallic. For all other tubes (chiral and zigzag) when tube indices $(n + m)/3$ is a whole number integer, the tubes are metallic, and otherwise, they are semiconducting. CNTs can in principle play the same role as silicon does in electronic circuits, but on a molecular scale where silicon and other standard semiconductors cease to work. SWCNT bundles

have been used to construct elementary computing circuits known as logic gates. Metallic nanotubes can have electrical current densities on the order of 1000 times that of silver and copper.

10.14.3.2 MECHANICAL

CNTs have superior resilience and tensile strength. They can be bent and pressed over a large angle before they begin to ripple or buckle, finally developing kinks. Until the elastic limit is exceeded, the deformations are elastic with the deformation disappearing when the stress is removed. It is envisioned that buildings and bridges built from them may sway during an earthquake rather than fracturing and crumbling. MWCNTs can easily slide past one another without friction resulting in a rotating bearing used in rotational motors.

10.14.3.3 FIELD EMISSION

When stood on end, electrified CNTs act as a lightning rod concentrating the electrical field at their tips. While a lightning rod conducts an arc of electricity to a ground, a nanotube emits electrons from its tip at a rapid rate. Because the ends are so sharp, the nanotube emits electrons at lower voltages than do electrodes made from other materials and their strength allow nanotubes to operate for longer periods without damage. Field emission is important in several industrial areas including lighting and displays. Commercial use of CNTs as field emitters has begun. Vacuum-tube lamps in six colors have been developed that are twice as bright as conventional light bulbs, longer lived, and at least 10 times more energy efficient as conventional light bulbs.

10.14.3.4 HYDROGEN AND ION STORAGE

While we can picture CNTs as being composed of hexagonal carbon atoms with lots of empty space between the carbons, atoms “thrown” against them generally just bounce off. Even helium atoms at an energy up to 5 eV do not readily penetrate the nanotube. Thus, the graphene sheet and CNTs are really membranes or fabrics that are one atom thick made of the strongest material that is also impenetrable (to a limit). Thus, CNTs can be used for hydrogen storage in their hollow centers with release being controlled allowing them to act as inexpensive and effective fuel cells.

10.14.3.5 CHEMICAL AND GENETIC PROBES

Nanotube-tipped atomic force microscopes can trace a strand of DNA and identify chemical markers that reveal DNA fine structure. A miniaturized sensor has been constructed based on coupling the electronic properties of nanotubes with the specific recognition properties of immobilized biomolecules through attaching organic molecules—handles—to these tubular nanostructures. In one study, the pi-electron network on the CNT is used to anchor a molecule that irreversibly adsorbs to the surface of the SWNT. The anchored molecules have a “tail” to which proteins, or a variety of other molecules, can be covalently attached. The result is that these molecules are immobilized on the sidewall of the nanotube with high specificity and efficiency. The molecule’s tail is tipped with a succinimidyl ester group, which is readily displaced when an amine group attacks the ester function, forming an amide bond. Thus, the CNTs are used as both highly sensitive probes and highly selective immobilizing sites that allow specific reactions to occur.

10.14.3.6 ANALYTICAL TOOLS

SWCNTs are being used as tips of scanning probe microscopes. Because of their strength, stability, and controllable and reproducible size, the tub probes allow better image fidelity and longer tip lifetimes.

10.14.3.7 SUPERCONDUCTORS

CNTs offer unique electronic properties due to quantum confinement. According to quantum confinement, electrons can only move along the nanotube axis. Metallic CNTs are found to be high-temperature superconductors.

10.14.4 HEALTH ISSUES

A major concern involves their possible toxicity. Research involving their potential and real toxic effects is just beginning. This is particularly important since these materials may become part of our everyday lives in many ways. Current results indicate that nanotubes can cross membrane barriers. If this is true, then access to our organs will occur. There is building biological evidence suggesting that under certain conditions nanotubes, of any origin, pose a real risk to our health.

Compounding the question of toxicity is the large variety of nanotubes potentially and really available each with its own toxicity profile. Further, the description of these various materials by name or other convention has yet to be settled.

A major concern involves their possible toxicity. Research involving their potential and real toxic effects is just beginning. This is particularly important since these materials may become part of our everyday lives in many ways. Current results indicate that nanotubes can cross membrane barriers. If this is true, then access to our organs will occur. There is building biological evidence suggesting that under certain conditions nanotubes, of any origin, pose a real risk to our health. Further, the description of these various materials by name or other convention has yet to be established.

10.14.5 POTENTIAL

While CNTs have a great potential, as evidenced by properties given in Table 10.8, currently large-scale production of single-stranded homogeneous CNTs has yet to be achieved. The properties given in Table 10.8 are for specially purified samples. Not only do CNTs come in different lengths, but also different number of walls, different diameters, and different twists and turns for the tubes, and typically they come bunched together this way. In fact, the semiconducting tubes have different twists than metallic tubes. Materials with “super” properties will require materials with homogeneity in structure. Progress is occurring to achieve these homogeneous tubes and much large-scale application of CNTs awaits this.

10.15 BITUMENS

The petroleum industry, including the commercial bitumen industry, was born in the United States in August 27, 1859, when Colonel Drake drilled a hole about 70 ft deep near Titusville, Pennsylvania, to “bring in” the first producing well. By 1908, Henry Ford began to mass-produce his Model “T” Ford creating an additional need for this petroleum in the form of gasoline. The distillation residue became more plentiful and a need for large-scale usage of bitumens increased.

Even so, the bitumens are a very old material. They were used in the waterproofing of the cradle that baby Moses was floated in. It was used by the ancient Egyptians in their mummification process. Bitumens were used in sand stabilization and for lighting the naval base by the Second Muslim Caliph, Omar ben Khattab, at Basra on Shattul-Arab on the West Coast of what is now Saudi Arabia around 640 AD.

Bitumens occur naturally or are formed as the residue in the distillation of coal tar, petroleum, etc. Industrially, the two most important bitumens are asphalt and coal tar. Asphalt is a brown to black tar-like variety of bitumen that again occurs naturally or is the residue of distillation. Coal tar is the black, thick liquid obtained as the residue from the distillation of bituminous coal.

Bitumens are examples of materials that have only an approximate structure. Bitumens are carbon-intense small polymers with molecular weights from about 200 to 1000 Da for coal tar with a calculated average number of carbons in a chain of about 15 to 70. Asphalt has a molecular weight averaging about 400–5000 Da with a calculated average number of carbons in a chain of about 30 to about 400. Thus, they are generally oligomeric to short polymers. Asphalt has a C/H ratio of about 0.7 while coal tar has a C/H ratio of about 1.5 approaching that of a typical hydrocarbon where the C/H ratio is about 2.



PICTURE 10.14 Asphalt fiberglass roofing shingle.

As with most nonpolar hydrocarbon-intense polymers, bitumens exhibit good resistance to attack by inorganic salts and weak acids. They are dark, generally brown to black, with their color difficult to mask with pigments. They are thermoplastic materials with a narrow service temperature range unless modified with fibrous fillers and/or synthetic resins. They are abundant materials that are relatively inexpensive, thus their use in many bulk applications.

At temperatures above the T_g , bitumens generally show Newtonian behavior. Below the T_g bitumens have rheological properties similar to elastomers.

Bitumens are consumed at an annual rate in excess of 75 billion pounds in the United States. Bitumens are generally used in bulk such as pavements (about 75%), and in coatings for roofs (15%), driveways, adhesive applications, construction, metal protection, etc., where the bitumen acts as a weather barrier. Asphalt shingles are made from bitumen embedded in usually a fiberglass mat covered on top with a colored synthetic ceramic grit. It is less expensive than tile or slate and the “fiberglass shingle” is among the most used roofing material in the United States (Picture 10.14).

Bituminous coatings are generally applied either hot or cold. Hot-applied coatings are generally either filled or nonfilled. Cold-applied coatings are generally either nonwater or water containing. In the hot-applied coatings, the solid is obtained through a combination of cooling and liquid evaporation, while in the cold-applied coatings, the solid material is obtained through liquid evaporation. One often used coating employs aluminum pigments compounded along with solvents. These coatings are heat reflective and decrease the energy needs of building using them. The aluminum-metallic appearance is generally more desirable than black, and the reflective nature of the aluminum reflects light that may damage the bitumen coating allowing the coating a longer useful life. Today, many of the bitumen coatings contain epoxy resins, various rubbers, and urethane polymers.

10.16 CARBON BLACK

Carbon black is another of the carbon-intensive materials. It is formed from the burning of gaseous or liquid hydrocarbons under conditions where the amount of air is limited. Such burning favors “soot” formation, that is, carbon black formation. It was produced by the Chinese over 1000 years ago. Today, it is produced in excess of 1.5 million tons annually in the United States. The most widely used carbon black is furnace carbon black. The particle size of this raw material is relatively large, about 0.08 μm . It is soft with a Mohs scale hardness of less than one.

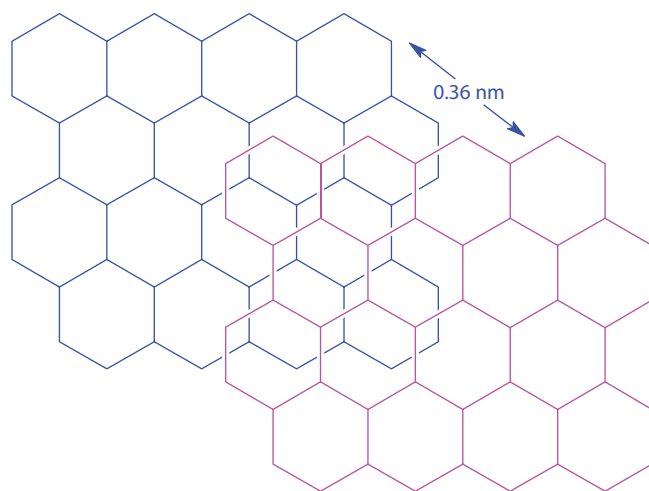


FIGURE 10.11 Sheets of carbon black.

In addition to carbon, carbon black also contains varying amounts of oxygen, hydrogen, nitrogen, and sulfur. A typical carbon black contains about 98% carbon, 0.3%–0.8% hydrogen, 0.3%–1.2% oxygen, 0.0%–0.3% nitrogen, and 0.3%–1% sulfur. The impurities in the water employed to quench the burning carbon is mainly responsible for the noncarbon and hydrogen content and the sulfur comes mainly from the feedstock.

While some describe the structure of carbon black as being small chainlike structures, recent information shows it as being somewhat graphite-like in structure where the parallel planes are separated by about 0.35–0.38 nm, always greater than the interlayer distance for graphite of 0.335 nm (Figure 10.11). The microstructure of carbon black has been studied extensively employing varying spectroscopies including ATE, high-resolution transmission electron microscopy, and x-ray diffraction. Various models have been developed to describe the average structure in greater detail. These models are related to the structure of graphite.

As with other polymeric materials, the surface structure is different from the bulk and is related to the conditions under which the material was manufactured. Since the material is formed in air, the surface is rich in oxygen. These oxygen atoms play an important role in the resulting carbon black properties. The surface can be modified using a variety of treatments. Heat treatments above 800°C act to increase the amount of crystallinity in the overall structure. Under inert conditions surface groups are modified and the amount of oxygen decreased with heating from 200°C to 1200°C. Plasma treatments are employed to modify the carbon black surface creating and destroying various functional groups in the presence of other reactants. Chemical oxidation is also employed to modify carbon black employing oxidizing agents such as air, nitric acid, and ozone. Surface grafting is also employed to provide desired surface functional groups.

The nature of the surface is especially important for carbon black since most applications employ the carbon black as an additive forming blends and alloys. These blends can be bound by simple physical contact or by chemical binding through formation of chemical bonding between the various phases.

A major use of carbon black is in rubbers. Incorporation of carbon black into a rubber matrix can result in an increase in strength-related properties such as abrasion resistance, viscosity, and modulus. Thus, carbon black is a reinforcing agent rather than simply an inexpensive additive. The reinforcing effect is dependent on the particle size, amount, aggregate structure, surface area, surface activity, etc. The reinforcing effect mainly occurs because of the interaction between the interfacial surfaces of the rubber matrix and the carbon black. Carbon blacks can be divided roughly as to being reinforcing (<35 nm) or semi-reinforcing (>35 nm) depending on the particle size. The antiabrasion of carbon black increases with increase in particle size.

Carbon black is the most important additive to rubber composing of between 30% and 70% of the bulk rubber product. Tire goods consume about 65% of the carbon black, mechanical goods another 25%, with only about 10% employed for nonrubber applications.

A typical tire rubber formulation for tire tread will contain various rubbers, mainly styrene-butadiene (50%) and *cis*-polybutadiene (12%), various processing aids (2%), softeners (3%), vulcanizing agent (mainly sulfur; 1%), accelerators, and reinforcing filler (viz., carbon black; 30%) so that by bulk, carbon black is the second most used material.

Of the 10% of carbon black used for nonrubber applications, about 35% is used for plastics, 30% for printing inks, 10% for coating, and 5% for paper. In plastics, carbon black enhances a variety of properties including UV shielding, electrical conductance, pigment, opacity, and mechanical properties. Plastics that use carbon black filler may contain only several percent to having over half of the weight being carbon black.

In xerography, carbon black is the most important pigment in printing or duplicating toner applications. Here, blackness, good dispersion, and needed electrical properties are provided by carbon black. Similarly, these properties are useful for applications in coatings, inks, and printing. Here though, rheological properties in liquid media are also important.

10.17 POLYSULFUR

Sulfur is present in the petrochemicals derived from once-living matter because of its presence in certain amino acids. Because of its removal from industrial waste, sulfur has been stockpiled and is available at a low price in large amounts. While the stable form of sulfur at room temperature is cyclooctasulfur, S_8 , linear polysulfur is formed on heating. Unfortunately, the thermodynamically stable form of sulfur is the cyclooctasulfur monomer and the polymer undergoes depolymerization after awhile. Methods have been studied to inhibit this reversal process. Some have involved the addition of olefins such as limonene, myrcene, and cyclopentadiene to the ends to inhibit the depolymerization. Such stabilized polysulfur has been incorporated into concrete and asphalt mixes to strengthen them. Concrete blocks, posts, and parking tire restrainers containing polysulfur are now being produced.

10.18 CERAMICS

The term “ceramics” comes from the Greek word *keramos*, which means “potter’s clay” or “burnt stuff.” While traditional ceramics were often based on natural clays, today’s ceramics are largely synthetic materials. Depending on which ceramic and which definition is to be applied, ceramics have been described as inorganic ionic materials and as inorganic covalent (polymeric) materials. In truth, many ceramics contain both covalent and ionic bonds and thus can be considered “to be or not to be” (shades of Shakespeare) polymeric materials. Many of the new ceramics, such as the boron nitriles and the silicon carbides, are polymeric without containing any ionic bonds.

Ceramics are typically brittle, strong, and resistant to chemicals such as acids, bases, salts, and reducing agents, and they are high melting. They are largely composed of carbon, oxygen, and nitrogen and made from silicates such as clay, feldspar, bauxite, and silica. But now ceramics contain other materials such as borides, carbides, silicides, and nitrides.

Ceramics are generally made by two processes—sintering and fusing. In sintering, the starting material is reduced to a powder or granular form by a series of crushing, powdering, ball-milling, etc. The ground preceramic material is then sized, separated according to particle size, using different-sized screens.

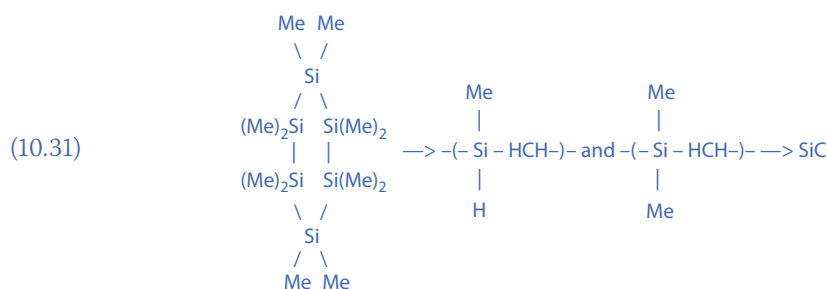
Ceramic material is generally shaped by pressing it into a form or through extruding, molding, jiggering, or slip-casting. Slip-casting uses a suspension of the preceramic material in water. The mixture must be dilute enough to allow it to be poured. Deflocculants are often added to assist in maintaining the suspension. The “slip” is poured into a plaster of Paris mold that absorbs water, leaving the finished shape. The preceramic material hardens next to the mold and surplus “slip” material poured off leaving a hollow item. At this point, the molded material is referred to as a “green body,” which has little strength. Coffee pots and vases are formed using this technique.

In jiggering, machines press the preceramic material into a rotating mold of desired shape. Dinnerware products are often made using jiggering.

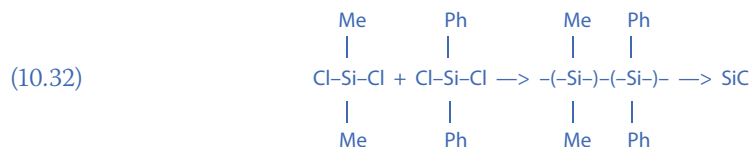
Abrasives and insulators are formed from simply pressing the preceramic material into a mold of desired shape. In extrusion, the preceramic material is forced through an opening in a “shaping” tool. Bricks and drainpipes are formed using extrusion.

After the product has dried, it is heated or fired in a furnace or kiln. Modern ceramics generally require certain heating schedules that include the rate and duration of heating and under what conditions such as in the presence or absence of air. This is similar to procedures used to produce carbon fibers where the heating schedule is critical to the end product’s properties.

In one approach, six-membered silicon-containing rings are pyrolyzed giving mixed carbosilane preceramic polymers through heating to 400°C and subsequently forming silicon carbides or poly(carbosilanes) at 800°C (10.31).



SiC fibers can be formed using dimethyl dichlorosilicon and diphenyl dichlorosilicon heated together (10.32).



Such “ceramic” fibers offer uniquely strong and resistant inexpensive materials including new ceramic composites that have great fracture toughness.

There are a number of other “non-oxygen” or nonoxide ceramics including phosphonitric chlorides (PN backbone), boron nitriles (BN), aluminum nitriles (AlN), titanocarbosilanes (Si–Ti–C backbone), and silazanes (Si–C–N backbones).

Many ceramic products are coated with a glassy coating called a glaze. The glaze increases the resistance of the material to gas and solvent permeability and makes the surface smoother in art objects used for decoration.

One group of advanced material ceramics are the zirconia ceramics (Picture 10.15). Most of these are based on zirconia (zirconium (IV) oxide) that contains small amounts of magnesia (magnesium oxide). They have bending strengths two to three times that of corundum and alumina, high fracture toughness (about five times that of corundum ceramics), high resistance to wear and corrosion, and high density (5.8 g/cc). They are used in the construction of shear blades in the textile industry, as plungers in the food and drink industry, as valves in the petroleum industry and as milling balls in the materials industry.

Zirconia exists in three solid phases (10.33):



The transformations between the monoclinic and tetragonal phases involve large and abrupt volume changes introducing fractures in the material. This is minimized through the use of di- and trivalent oxides of the cubic symmetry such as calcium oxide and magnesium oxide. This results in a lowering of the transition temperatures (M → T and T → C) and also lowers the expansion coefficient of the zirconia and the subsequent volume changes associated with the phase changes reducing ceramic fracturing. The addition of calcium oxide or magnesium oxide is said to “stabilize” the ceramic.



PICTURE 10.15 Zirconia ceramic spheres and plungers.

Strength, brittleness, and solvent permeability properties are limited because of lack of control of the ceramic composition on a macro- and microlevel. Even small particle sizes are large compared with the molecular level. There have been a number of attempts to produce uniform ceramic powders including the sol-gel synthesis where processing involves a stable liquid medium, coprecipitation where two or more ions are precipitated simultaneously. More recently, Carraher and Xu have used the thermal degradation of metal-containing polymers to deposit metal atoms and oxides on a molecular level.

10.19 HIGH-TEMPERATURE SUPERCONDUCTORS

10.19.1 DISCOVERY OF THE 123-COMPOUND

In early 1986, George Bedor and K. Alex Muller reported a startling discovery—a ceramic material, La-Ba-Cu-O , lost its resistance to electrical current at about 30 K. This was the first report of a so-called high T_c superconductor. Intensive efforts were then concentrated on substituting the component ions with similar elements on both the La and Ba sites. The first success was reported by Kishio et al. with an $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ system that exhibited a higher T_c to about 37 K. Then the substitution on the La sites led Wu and coworkers to find another superconductor, the Y-Ba-Cu-O system with a T_c of 93 K in February 1987. This finally broke the technological barrier that would allow superconductivity at temperatures above liquid nitrogen. The superconducting phase was identified as $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ (commonly referred to as the 123-compound). The 123-compound was the first of the 90 K plus superconductors to be discovered and it has been the most thoroughly studied.

10.19.2 STRUCTURE OF THE 123-COMPOUND

The structure of the 123-compound is related to that of an important class of minerals called perovskites. These minerals contain three oxygen atoms for every two metal atoms. It has six metal atoms in its unit cell and would be expected to have nine oxygens if it were an ideal perovskite. In fact, it has, in most samples, between 6.5 and 7 oxygens. In other words, in comparison to an ideal perovskite, about one-quarter of the oxygens are missing. The unit cell can be thought of as a pile of three cubes. Each cube has a metal atom at its center: barium in the bottom

cube, yttrium in the middle one, and barium in the top one. At the corners of each cube, a copper would be surrounded by six oxygens in an octahedral arrangement linked at each oxygen in an ideal perovskite. Each barium and yttrium would then be surrounded by 12 oxygens. But x-ray and neutron diffraction studies have shown that the unit cell does not conform to this simple picture because certain oxygen positions are vacant. All oxygen positions in the horizontal plane containing yttrium are vacant. The other vacancies are located in the top and bottom Cu–O planes.

The two copper oxide layers can be considered as polymeric since the covalent character is in the same range as for the carbon fluoride bond in Teflon. Thus, the 123-superconductors consist of two types of polymeric copper oxide layers held together by ionic bonding metals such as barium and yttrium. This theme of polymeric layers held together by ionic bonding to metals is common in the silicates and other minerals.

10.20 ZEOLITES

At least three major themes are helping drive polymer synthesis and use of polymers today. These involve synthesis and assembling on an individual scale (nanolevel), synthesis in confined spaces (selected inorganic zeolites and biological syntheses), and single-site catalysis (both selected biological and synthetic polymer synthesis). Superimposed on this is the applications aspects including the human genome/biomedical and electronic/communications.

Zeolites include a whole group of aluminosilicates with an approximate formula of $\text{Si}_x\text{Al}_y\text{O}_{4x+y}$. With respect to the type of bonding, zeolites can be divided into three groups. The natrolite group (mesolite, thomsonite, edingtonite, natrolite) consist of structures built up from rings of four SiAlO_4 tetrahedral linked together into chains with fewer linkages between the chains so that cleavage along the chain direction is preferred. These materials generally have a fibrous character. In the heulandite group (stilbite, epistilbite, and heulandite), the SiAlO_4 tetrahedra form sheets of six-membered rings with few linkages between the sheets. These materials are mica-like in behavior. The third group, the so-called framework zeolites, have the density of bonding similar in all three directions. This group includes most of the zeolites mentioned later.

Framework zeolites can be described as aluminosilicates composed of tetrahedra linked by the sharing of oxygen atoms into rings and cages that can accommodate water molecules, metallic ions, and selected organic molecules. While there are a variety of structures, the framework zeolites can be briefly described as having an open arrangement of corner-sharing tetrahedra where the SiO_4 are partially replaced by AlO_4 units where there are enough cations present to be neutral. There are well over 100 different synthetic and natural framework zeolites known today with more being found. Magic-angle NMR indicates that there are five distinct zeolite groups where $n = 0-4$ for $\text{Al}(\text{AlO})_n(\text{SiO})_{4-n}$. The open structures give materials with lower densities (on the order of 2.0–2.2 g/mL), as expected, than similar materials with closed structures such as feldspar (density about 2.6–2.7 g/mL).

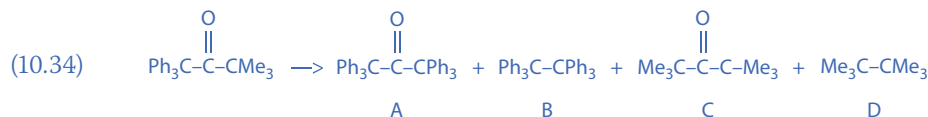
Molecular sieves was the name first given to framework zeolites dehydrated by heating in vacuum to about 350°C because of their ability to capture and remove water and certain other species. Today, other materials, such as microporous silicas and aluminum phosphate, are also employed as molecular sieves.

Syntheses that occur within confined spaces typically give products with a specificity that is not available by other modes. The specificity may be general such as in the case of the synthesis of lignins in plants where synthesis between plant layers produces a largely 2D material with only an average structure. It may be highly but not totally selective as in the case of zeolites and hollow nanofibers. Or it may be essentially totally selective as in the case of many of the biologically important proteins and nucleic acids where both spatial and electronic interactions act to give a highly “pre-ordained” structure.

Zeolites and related ordered clay-associated materials have been suggested to be involved in the initial primeval synthesis of basic elements of life. They are also being involved in the synthesis of a number of polymeric and nonpolymeric materials. Zeolites come in a variety of forms with differing shapes and sizes with researchers associating the particular size and shape with a

particular desired synthesis. This is somewhat akin to the considerations that are made in effectively employing crown phase transfer agents and related materials.

Zeolites have been employed in the preferential synthesis of optically active sites and in determining the particular products formed from certain reactions. In looking at the products formed from the decomposition and reformations involving the unsymmetrical ketone, the major products are a combination of products listed as follows (10.34).



Employing a single zeolite that selectively accommodates the Me_3C radical results in a preferential formation of D and little C because of preferential diffusion of the Me_3C radical as it is formed with the other radicals being “washed” past. The use of two zeolites in conjunction, one preferentially accepting the Me_3C radical and the second accepting the Ph_3C radical, results in the preferential formation of B and D.

An additional consideration involves matching the so-called hardness or flexibility of the confined space. Zeolites offer hard or inflexible confined spaces whereas liquid crystals and some other polymer media offer softer confined spaces. While the zeolites offer a “safe haven” for selected species enabling the hosted species a relatively long existence, they do not allow for ready movement and mixing. By comparison, a more flexible container such as specially designed polyethylenes allows a more flexible environment that allows for variations in the product sizes and shapes and some assembling to occur within the more flexible confines. Thus, the reaction of 1-naphthyl esters was carried out in an appropriate zeolite and appropriate polyethylene. In solution, eight products are formed. In the zeolite only one product, the result of a specific geminate-pair recombination, is formed. In the polyethylene, several products are formed, primarily the isomeric products of geminate-pair recombination.

SUMMARY

1. Inorganic polymers are widely employed in the construction and building businesses, as abrasives and cutting materials, as fibers in composites, as coatings and lubricants, and as catalysts. They also serve as the basis of rocks and soils.
2. Portland cement is the least expensive, most widely used synthetic polymer. It has a complex (short-range order and long-range disorder; average structure), 3D structure.
3. There are many specialty cements including reinforced concrete, lightweight concrete, prestressed concrete, gypsum, and heavy glass.
4. Silicates are among the most widely found materials on the face of Earth. They form the basis for much of the soil, sand, and rocks with most of this being of the crystalline variety of silicates. As amorphous materials, they are found as the fiber material in fiberglass, as window glass, and as a whole host of specialty glasses including safety glass, borosilicate glasses, lead (or heavy) glasses, colored glasses, and glazes. Glass can be shaped by drawing, pressing, casting, and blowing. Most of these glasses have the approximate structure of SiO_2 or silicon dioxide. Many of the rocks are present in crystalline silicate forms as quartz and feldspar. Today, the sol-gel technique is important in making many materials including aerogels, among the least dense solids known today. In nature, silicates are found as polymeric sheets such as asbestos, 3D materials such as the zeolites, and linear materials.
5. There are many widely used carbon polymers. These include the hardest known material diamond; graphite, a sheet material with little strength holding together the sheets; carbon fibers, used in high-strength composites; CNTs, one of the most important new materials in the twenty-first century; bitumens, used in asphalt; and carbon black, widely used as a filler material. Diamonds structurally have a carbon at the center of a

tetrahedron composed of four other carbon atoms. They can be industrially synthesized and used for cutting and shaping. Graphite occurs as sheets of hexagonally fused benzene rings. The bonds holding the fused benzene rings together are covalent bonds while the bonding between the sheets results from the weaker overlapping of pi-electron orbitals. Thus, many of the properties of graphite are anisotropic. The weak forces holding the sheets together are responsible for its “slipperiness.” Graphite is commercially made from charcoal or coke.

6. Many ceramics are partially polymeric in structure. These include the new superconductive materials that exist as polymeric sheets connected by metal ions similar to many of the silicate sheets.

GLOSSARY

Alumina: Aluminum oxide.

Annealing: Subjecting a material to near its melting point.

Asbestos: Group of silica-intensive materials containing aluminum and magnesium that gives soft, threadlike fibers.

Asbestosis: Disease that blocks the lung sacks with thick fibrous tissue.

Borosilicate glass: Relatively heat-shock-resistant glass with a small coefficient of thermal expansion, such as Kimax and Pyrex.

Calcium-aluminate cement: Contains more alumina than Portland cement.

Chrysotile: Most abundant type of asbestos.

Concrete: Combination of cement, water, and filler material such a rock and sand.

Diamonds: Polymeric carbon where the carbon atoms are at centers of tetrahedra composed of four other carbon atoms; hardest known natural material.

Feldspars: Derivatives of silica where one-half to one-quarter of the silicon atoms are replaced by aluminum atoms.

Fibrous glass (fiberglass): Fibers of drawn glass.

Float glass: Glass made by cooling sheets of molten glass in a tank of molten tin: most common window glass is of this type.

Glass: Inorganic product of fusion that has been cooled to a rigid condition without crystallization; most glasses are amorphous silicon dioxide.

Glass sand: Impure quartz crystals.

Glaze: Thin, transparent coatings fused on ceramic materials.

Granite: Hard crystalline rock containing mainly quartz and feldspar.

Graphite: Polymeric carbon consisting of sheets of hexagonally fused rings where the sheets are held together by weak overlapping pi-electron orbitals; anisotropic in behavior.

Gypsum: Serves as the basis of plaster of Paris, Martin’s cement, etc.; shrinks very little on hardening and rapid drying.

High-temperature superconductors: Polymeric copper oxide layers containing metal atoms that hold them together, which are superconductors above the boiling point of liquid nitrogen.

Inorganic polymers: Polymers containing no organic moieties.

Kaolinite: Important type of asbestos.

Lead glass (heavy glass): Glass where some or all of the calcium oxide is replaced by lead oxide.

Lime: calcium carbonate from oyster shells, chalk, and marl.

Magnesia cement: Composed mainly of magnesium oxide; rapid hardening.

Optical fibers: Glass fibers coated with highly reflective polymeric coatings; allows light entering one end to pass though the fiber to the other end with little loss of energy.

Piezoelectric effect: Materials that develop net electronic charges when pressure is applied; sliced quartz is piezoelectric.

Portland cement: Major 3D inorganic construction polymer containing calcium silicates, lime, and alumina.

Precast concrete: Portland concrete cast and hardened prior to being taken to the site of use.

Prestressed concrete: Portland concrete cast about steel cables stretched by jacks.

Quartz: Crystalline forms of silicon dioxide; basic material of many sands, soils, and rocks.

Reinforced concrete: Portland concrete cast about steel rods or bars.

Safety glass: Laminated glass; sandwich containing alternate layers of soda-lime glass and poly(vinyl butyral).

Sand: Loose grains of minerals or rocks larger than silt but smaller than gravel.

Sandstone: Granular quartz.

Silica: Based on SiO_2 ; finely ground sand.

Silicon glass: Made by fusing pure quartz crystals or glass sand; high melting.

Soda: Na_2O .

Soda ash: Na_2CO_3 .

Soda-lime glass: Most common glass; based on silica, soda, and lime.

Soil: Contains mineral and organic particles; majority by weight is sand.

Tempered safety glass: Single piece of specially treated glass.

Tempering: Process of rapidly cooling glass resulting in an amorphous glass that is weaker but less brittle.

Vitreous enamels: Thin, normally somewhat opaque-colored inorganic coatings fused on materials.

Vycor: 96% silicon glass; made from silicon and boron oxides; best variety is called fused quartz.

EXERCISES

1. What properties of glass correspond to those of organic polymers?
2. Why is Portland cement an attractive large-bulk use building material?
3. Name five important synthetic inorganic polymers. Name five important natural inorganic polymers.
4. Describe what is meant by 3D polymers. Name five important 3D polymers. Name two general properties typical of 3D polymers.
5. Why are specialty cements and concretes necessary?
6. What is intended by the comment that “glass is a supercooled liquid”?
7. Briefly describe techniques employed to shape glass.
8. Why are specialty glasses important in today’s society?
9. Name two important inorganic fibers employed with resins to form useful materials.
10. Which would you predict to be more brittle: quartz, fibrous glass, or window glass?
11. Briefly describe the piezoelectric effect.
12. We do not live in a risk-free society. Discuss this statement in terms of asbestos.
13. What does anisotropic behavior mean? Why does graphite exhibit anisotropic behavior?
14. Briefly compare the structures of diamond and graphite.

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Reactions of Polymers

Reactions of polymers in nature and industry are widespread. In nature, reactions of polymers serve as the basis for information transfer, synthesis of needed biomaterials, and degradation of biomaterials and, in fact, are at the core of life itself. Nature also reacts with synthetic polymers as they age, degrade, cross-link, etc. Synthetic polymers also serve as the basic material for the production of many important fibers, elastomers, and plastics. The nature of these reactions is governed similarly whether the source and site of a polymer is nature or man-made. There are some differences especially with respect to the precision of the interaction and predicted outcome. Some polymer interactions, such as those that transfer information, must occur with a very high degree of precision for each and every incident. By comparison, naturally induced degradation of natural and synthetic polymers through weathering occurs through general steps that can be described in some statistical manner.

Reactions of synthetic polymers often mimic similar reactions involving small molecules where size is the main difference. There are some exceptions such as where near groups may hinder or assist in the reaction where differences occur. Here, the main differences are often kinetic, though some geometrical differences are found for specific cases. A reaction where the rate of reaction in polymers is enhanced by the presence of neighboring groups is called anchimeric assistance.

While there are many possible routes, most degradation can be described as occurring through two general routes—unzipping and random scission. Polymers such as polysiloxanes and polysulfur undergo unzipping reactions forming preferred internal cyclic products unless the end group is capped in such a manner as to discourage unzipping. In unzipping, one end begins to *unzip*, and this process continues down the chain until it is completed. Random scission is the normal degradation pathway for most natural (such as polycarbohydrates) and synthetic polymers. Here, a long chain is attacked at some site, normally one that is exposed and of the exposed sites, one that is stressed. Thus, while random scission implies a random statistical manner of chain breakage, superimposed on this are more complex considerations of exposure and stress and the likelihood that a particular site is susceptible to that particular type of bond breakage.

This chapter describes many of the important reactions of polymers. Synthesis and curing (cross-linking) of polymers and telomerization are chemical reactions of polymers that have been discussed in previous chapters.

11.1 REACTIONS WITH POLYOLEFINS AND POLYENES

As with other carbon-, hydrogen-, and oxygen-containing materials, the main products of combustion in the presence of oxygen are water and carbon dioxide. Such polymers can be reacted with various reactants giving products analogous to those obtained from small alkanes and alkane-intense compounds. The moderating conditions between reactions of small molecules and polymers involve contact between the polymer segments and the reactants.

Polyolefins, like simple alkanes, can be chlorinated by chlorine giving hydrogen chloride and chlorinated products such as Tyrin, used as plasticizers and flame retardants, and poly(vinyl dichloride) that has better heat resistance than poly(vinyl chloride) (PVC) and is used for hot water piping.

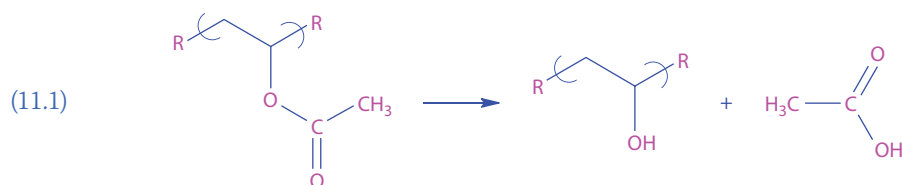
Reactions with polyenes are similar to the reactions of alkenes. Thus, Hermann Staudinger found that polyenes such as *Hevea brasiliensis* could be hydrogenated, halogenated, hydrohalogenated, and cyclized. This classic work was done in the early 1900s. In fact, Berthelot hydrogenated *H. Brasiliensis* in 1869. Chlorinated rubber (Tornesit and Parlon) is produced by the chlorination of rubber giving products with varying amounts of chlorine and is used for the coating of concrete. Hydrohalogenation of *H. brasiliensis* gives a product (such as Pliofilm) that is a packaging film.

The product obtained by the partial hydrogenation of polybutadiene (Hydropol) has been used as a wire coating, and a saturated ABA copolymer (Kraton) is produced by the hydrogenation of the ABA block copolymer of styrene and butadiene.

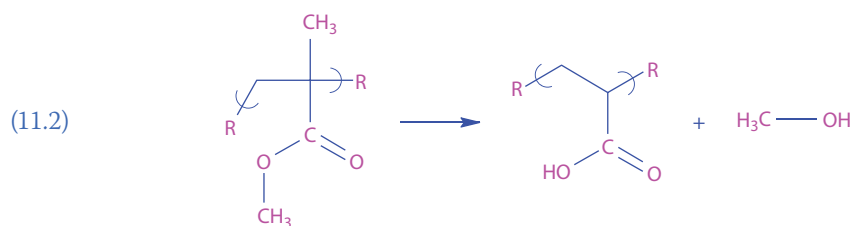
11.2 REACTIONS OF AROMATIC AND ALIPHATIC PENDANT GROUPS

Polymers with aromatic pendant groups, such as polystyrene (PS), undergo all of the characteristic reactions of benzene including alkylation, halogenation, nitration, and sulfonation. PS has been sulfonated by fuming sulfuric acid with cross-linked products used as ion-exchange resins. Living polymers (cation propagation) are used to form a variety of products with hydroxyl and dihydroxyl products forming telechelic and macromers. Polyaminostyrene is formed from the nitration of PS. These polyaminostyrene products can be diazotized giving polymeric dyes.

Esters such as poly(vinyl acetate) (PVAc) may be hydrolyzed producing alcohols such as poly(vinyl alcohol) (PVA; Equation 11.1), which will have the same DP as the ester. In truth, PVAc does not totally hydrolyze, but with reasonable effort, the extent of hydrolysis is greater than 90%. Since PVAc is not water soluble, but PVA is, the extent of water solubility is dependent on the extent of hydrolysis:



Esters of poly(carboxylic acids), nitrites, and amides may be hydrolyzed to produce poly(carboxylic acids). Thus, polyacrylonitrile, polyacrylamide, or poly(methyl acrylate) may be hydrolyzed producing poly(acrylic acid) (Equation 11.2):



Poly(acrylic acid) and partially hydrolyzed polyacrylamide are used for the prevention of scale in water used for boilers and as flocculating agents in water purification.

Neutralization of ionic polymers, such as poly(acrylic acid), causes the now fully negatively charged carboxylate groups to repel one another, resulting in the chain changing conformation from that of a free-draining random shape to that approaching a rigid rod. This increase in length results in an increase in polymer viscosity with the extent of viscosity increasing depending on the fraction of ionic groups present. Addition of salts, such as sodium chloride, allows the negatively charged chains to return to a more random conformation.

Some of the largest polymers, with molecular weights of the order of 10–15 million daltons, contain sodium acrylate and acrylamide groups. Simple stirring can result in chain breakage

for these extremely high molecular weight chains. Copolymers containing sodium acrylate and acrylamide groups are used in tertiary oil recovery and in water purification.

11.3 DEGRADATION

Here, the term degradation includes any change, decrease, in polymer property because of the impact of environmental factors, namely, light, heat, mechanical, and chemicals. Seven polymers represent the majority of the synthetic polymers. These are the various polyethylenes (PE), polypropylene (PP), nylons, poly(ethylene terephthalate) (PET), PS, PVC, and polycarbonate (PC). Each of these has their own particular mode of degradation. Even so, there are some common generalities for the condensation (PET, PC, nylons) and vinyl (PE, PP, PS, PVC) polymers.

Some reactions on polymers are intended and give a material with different desired properties. The (positive) modification of polymers is an area of vigorous activity. Other reactions on polymers are unintended and generally result in a material with unfavorable properties. These are also actively studied to understand and prevent degradation. Some of these degradation reactions are covered elsewhere. Here, we will focus on some general concepts. Degradation can be promoted by many means and any combination of means. The major means of polymer degradation are given in Table 11.1.

Backbone chain scission degradation can be divided as occurring via depolymerization, random chain breakage, weak-link or preferential site degradation, or some combination of these general routes. In depolymerization, monomer is split off from an activated end group. This is the opposite of the addition polymerization and is often referred to as “unzipping”:



Chain scission is similar to the opposite of stepwise polycondensation where units are split apart in a random manner:



Depolymerization can result in backbone degradation and/or in the formation of cyclic (Section 10.12) or other products. The thermal degradation of PVA and PVC occurs with the splitting out of water or HCl followed by a combination of further chain degradation to give finally small products and formation of complex cyclic products. Elimination of HCl further accelerates additional HCl elimination and increased property loss. PVC degradation is decreased by the addition of agents that impede degradation such as those that neutralize HCl, trap free radicals, and/or react with the forming double bonds to impede further depolymerization. Commercial PVC often contains organotin or antimony mercaptide compounds that act as stabilizers.

TABLE 11.1 Major Synthetic Polymer Degradative Agents

Degradation Agent	(Most) Susceptible Polymer Types	Examples
Acids and bases	Heterochain polymers	Polyesters, polyurethanes
Moisture	Heterochain polymers	Polyesters, nylons, polyurethanes
High-energy radiation	Aliphatic polymers with quaternary carbons	Polypropylene, LDPE, PMMA, poly(alpha-methylstyrene)
Ozone	Unsaturated polymers	Polybutadienes, polyisoprene
Organic liquids/vapors	Amorphous polymers	
Biodegradation	Heterochain polymers	Polyesters, nylons, polyurethanes
Heat	Vinyl polymers	Poly(vinyl chloride), poly(alpha-methylstyrene)
Mechanical (applied stresses)	Polymers below T_g	

In general, for vinyl polymers thermal degradation in air (combustion) produces the expected products of water, carbon dioxide, and char along with numerous hydrocarbon products.

Most polymers are susceptible to degradation under natural radiation, sunlight, and high temperatures even in the presence of antioxidants. Thus, LDPE sheets, impregnated with carbon black, become brittle after exposure to 1 year's elements in South Florida. HDPE, while more costly, does stand up better to these elements, but again after several seasons, the elements win and the HDPE sheets become brittle and break. Long-term degradation is often indicated in clear polymers by a yellowing and a decrease in mechanical properties.

Most polymers are subject to oxidative degradation, particularly in the presence of other *enticers* such as heat, a good supply of air, various catalysts, high-energy radiation including UV and higher energy visible light, and mechanical stressing that not only exposes additional polymer to the *elements* but also brings about the actual breakage of bonds subsequently leading to additional breakdown.

While polymers that contain sites of unsaturation, such as polyisoprene and the polybutadienes, are most susceptible to oxygen and ozone oxidation, most other polymers also show some susceptibility to such degradation including natural rubber, PS, PP, nylons, PE, and most natural and naturally derived polymers.

Because of the prevalence of degradation by oxidation, antioxidants are generally added. These antioxidants are generally compounds that readily react with free radicals or those that may act to lessen the effects of *enticers* such as UV radiation.

Mechanical degradation, while applied on a macrolevel, can result not only in chain rearrangement but also in chain degradation. Such forces may be repetitive or abrupt and may act on the polymer while it is in solution, melt, elastic, or below its T_g . Passage of polymer melts through a tiny orifice for fabrication purposes can result in both chain alignment and chain breakage. In the case of rubber, mastication of the elastomer, breaking polymer chains, is intentional allowing easier deformation and processability. While shearing itself can result in chain breakage, chain breakage is often associated with localized heat buildup that is a consequence of chains rubbing together. (molecular friction).

Most heterochained polymers, including condensation polymers, are susceptible to aqueous associated acid or base degradation. This mode of degradation is referred to as hydrolysis. This susceptibility is due to a combination of the chemical reactivity of heteroatom sites and to the materials being at least wetted by the aqueous solution allowing contact between the proton or hydroxide ion to occur. Both of these factors are related to the difference in the electronegativity of the two different atoms resulting in the formation of a dipole that acts as a site for nucleophilic/electrophilic chemical attack and that allows polar materials to come in contact with the proton or hydroxide ions. Such polymers can be partially protected by application of a thin film of hydrocarbon polymer that acts to repel the aqueous solutions.

Enzymatic degradation is complex and not totally agreed upon. Microbes have enzymes, some of which are capable of breaking selected bonds such as those that appear naturally—including amide, ester, and ether linkages—and can include those that appear in synthetic materials. While a purpose of these enzymes is to digest nutrients for the host, when polymers with susceptible linkages come in contact with a microbe that contains appropriate enzymes, polymer degradation can occur. While often similar to acid- and base-associated degradations, enzymatic degradations are more specific bringing about only specific reactions. Even so, it is often difficult to differentiate between the two and both may occur together.

Some polymer deterioration reactions occur without loss in molecular weight. These include a wide variety of reactions where free radicals (most typical) or ions are formed and cross-linking or other non-chain scission reaction occurs. Cross-linking discourages chain and segmental chain movement. At times this cross-link is desired such as in permanent press fabric and in elastomeric materials. Often unintended cross-links bring about an increased brittleness beyond that desired.

Some degradation reactions occur without an increase in cross-linking or a lessening in chain length. Thus, minute amounts of HCl, water, ester, etc., elimination can occur with vinyl polymers giving localized sites of double bond formation. Because such sites are less flexible and because such sites are more susceptible to further degradation, these reactions are generally considered as unwanted.

Natural polymers utilize a combination of primary and secondary forces and bond angles and distances to form polymers with both long-range (multimacromolecular) and short-range structures with both structures essential for the *proper* functioning of the macromolecular structure. While most effort focused on what is referred to as primary and secondary structures (short-order structure control), work is just beginning on developing the appropriate structure control to allow tertiary and quaternary structural control (long-range control).

Self-assembled structures normally are the result of what are often referred to as weaker force interactions that include van der Waals forces, pi–pi interactions, and capillary interactions. Structures that successfully form ordered structures often take advantage of not only these short-range attractive forces but also of longer range repulsive forces. Almost all of these structures have some thermodynamic stability with the overall structure more stable than the unassembled parts. These driving forces make the structures especially susceptible to small variations in the conditions leading to ready reversibility.

Several strategies are being developed that allow this long-range control including the use of secondary forces to hold in place monomers that subsequently will be polymerized *in place*. In another approach, already molecular *architected* templates are employed to hold the polymer, prepolymer, or monomers in the desired shape with subsequent reactions and interactions enacted producing a material with a somewhat robust tertiary and quaternary structure. Some of these *molecular molds* are being produced using nanotechnology.

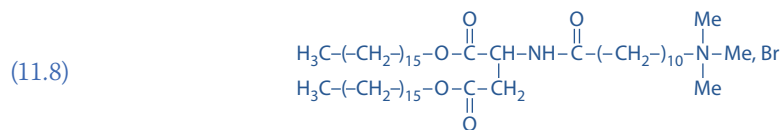
Self-assembly tendencies are apparent in the simple crystallization of inorganics and organics. Structure, size, and chemical tendencies (such as *like-liking-like* and *unlikes* repelling, secondary and primary bonding tendencies) are all involved. Proteins *self-assemble* in a much more diverse manner than so-called “simple” crystallization of common organics and inorganics. As noted earlier, we are just beginning to understand the nuances involved with the self-assembling, formation of giant macromolecules including organizations such as those present in the cells of our bodies. We are beginning to understand the major factors involved in making the cell membranes and are starting to mimic these features to form synthetic biological-like membranes. We are using self-assembling concepts and approaches to develop a large number of interesting and potentially useful macromolecular materials.

One of the applications of molecular self-assembling is the formation of ultrathin films using both synthetic and natural surfaces as two-dimensional templates. As noted earlier, the same chemical and physical factors that we recognize in other areas are at work here. We will begin considering the formation of a simple bilayer membrane such as that present in natural cell membranes. Using the concept of like-liking-like and unlikes rejecting one another, the orientation of molecules with two different polar environments will vary depending upon the particular environment in which they are placed. For a common soap molecule with hydrophilic and hydrophobic ends, the like ends will congregate together and will reside either internally together or externally together. This is exactly the same concept as given in most general chemistry texts when considering the formation of micelles in commercial detergents. In the presence of water, the hydrophilic ends will face outward, and in a nonpolar organic solvent, the polar ends will face inward. Researchers have extended these simple concepts to include specially designed molecules that contain not only the heads and tails but also spacers, conductors, and to vary the flexibility of the various parts of the molecule, spacing and number of heads and tails, etc.

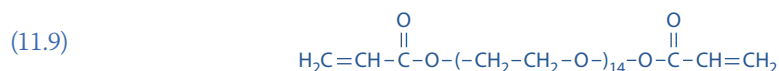
An important concept in the creation of some of these structures is that a primary driving force is the solute–solvent immiscibilities (energy; enthalpic). Thus, the magnitude of the cohesive energy of the solute may be a secondary factor in determining these supermolecular or supramolecular structures for such systems.

The self-assembling character of bilayer membranes is demonstrated by the formation of free-standing cast films from aqueous dispersions of synthetic bilayer membranes. The tendencies for association are sufficiently strong as to allow the addition of *guest* molecules (nanoparticles, proteins, and various small molecules) to these films where the connective forces are secondary in nature and not primary. Synthetic polymer chemists have made use of these self-assembling tendencies to synthesize monolayer films. Essentially a monomer that contains both reactive groups and hydrophobic and hydrophilic areas is *cast* onto an appropriate

template that *self-assembles* the monomer, holding it for subsequent polymerization. Thus, a bilayer structure (11.8) is formed by



The bis-acrylate monomer (11.9)



is accommodated by this bilayer. The bis-acrylate is photopolymerized. While there is some change in the particular bond lengths, the bilayer still holds on and a coherent film is formed. The bilayer template is subsequently washed away by addition of methanol leaving a flexible, self-supporting film. Polymerization can also result in the creation of different bond lengths that can act to release the newly formed monolayer. Multilayered structures can be made by simply allowing the outer surface of one monolayer to act as the template for the next monolayer.

Inorganics can also be synthesized and used as templates. Thus, controlled siloxane networks were formed when dispersions of alkoxysilanes (such as $(\text{MeO})_3\text{SiMe}$) are mixed with the suitable template matrices. Ultrafine particles of metal oxides can be used as starting materials for the formation of metal oxide films. For instance, a mixture of a double-chained ammonium amphiphile and an aqueous solution of aluminum oxide particles (diameter about 10–100 nm) gives a multilayered aluminum oxide film when calcinated at over 300°C.

Metal–ligand structures, such as porphyrin-based structures, are able to *control* the geometry of forming superstructures. The interactions between the various internally chelated porphyrin metals and a combination of the planarity and pi–pi interactions between the porphyrin rings drive the resulting structures. Connecting groups can act as spacers or act as additional geometry-determining features. Smaller metal-based groups have been used to self-assemble structures such as nanocages that can have within them molecules that give the combination cage and captive molecule unique chemical and electrical environments. A nanocage has been formed using six *cis*-protected palladium II nitrate molecules and four tridentate tripyridyl molecules. These structures, unlike other self-assembly molecules considered here, have primary bonds as major contributors to the self-assembly process.

Graphite and carbon fibers have been used as templates. Thus, nylon 6 has been polymerized on a graphite matrix. Such syntheses of polymers in the presence of a solid template where the solid acts as a template have been described as polymerized-induced epitaxy. The monomer and resulting film is adsorbed on the template surface through only van der Waals forces. After polymerization, the polymer is washed from the template. The recovered polymer retains special structural features introduced by the template.

Block copolymers with amphiphilic groups have been used to give molecules with several *levels* of molecular architecture. Thus, a block copolymer of styrene and 4-vinylpyridine and long-tailed alkylphenols contains polar groups in the backbone that associate with the alkylphenol chains forming hydrogen bonds resulting in a bottlebrush-like structure. If the alkyl tails on the polymer are strongly repulsed by the amphiphilic portions, microphase separation between the tails and the rest of the copolymer results. Here, the alkylphenol portion, which is hydrogen bonded to the vinylpyridine blocks, separates as a microphase inside the poly(4-vinylpyridine) block domains. If the copolymer is heated, the bottlebrush structure undergoes an order–disorder transition around 100°C and a second order–order transition about 150°C as the amphiphilic alkylphenol chains diffuse into the PS-rich domains and cylindrical structures are formed.

While much of the emphasis on inter- and intramolecular interactions, secondary bonding, and forces associated with association and dissociation involves attractive forces, we are finding that phobic effects are also important and for some systems are actually the major factors. Briefly, this can be described by such sayings as “the enemy of my enemy is my friend” or “given

the choice between bad and worse, bad wins out.” Formation of many self-assemblies is due in large measure to such phobic factors.

As we learn more about what drives molecular shapes, we are finding more applications utilizing this information in designing, on a molecular level, oligomeric and polymeric chains. It is also becoming more apparent to us that we have been forming organized structures without knowing it. While simple layered and linear structures are generally employed to describe the concept, the self-assembling approach holds for any two- and three-dimensional structure under the appropriate conditions. As in many of the areas of research, the potential is only limited by our imagination.

Considering only Lewis acid–base or donor–acceptor interactions, we can envision a hydrogen bond donor site such as an alcohol, acid, thiol, or amine and an acceptor site such as a carbonyl oxygen on another molecule or part of the molecule. These components will bind with one another, acting either to bind the molecules containing the two differing bonding sites or, if the two sites are on the same molecule attempt to contort, twist the molecule allowing the preferred bonding to occur.

Synthetic shapes are generally limited to sheets and polyhedral structures. Yet nature produces a much wider variety of shapes including curves, spirals, ripples, bowls, pores, tunnels, spheres, and circles. We are beginning to master such shapes. We are beginning to make these shapes based on especially grown shapes that act as templates for further growth. For instance, Geoffrey Ozin and coworkers mixed together alumina, phosphoric acid, and decylamine in an aqueous solution of tetraethylene glycol. After a few days, millimeter-sized aluminophosphate solid spheres and hollow shells were formed with the surfaces sculpted into patterns of pores, meshes, ripples, bowls, etc. A decylammonium dihydrogen phosphate liquid crystal phase was formed, and this surfactant, along with the glycol, was forming bilayer vesicles. The vesicles acted in different ways with some fusing to one another, others splitting apart or collapsing giving a variety of structures. Thus, appropriate conditions can be selected that favor certain template structures producing an array of geometric structures. Further, the templates themselves can be used to make selective separations. In a related study the group employed a silica precursor, tetraethyl orthosilicate. Here, the orthosilicate units assembled together forming micelles that in turn acted as liquid-seed crystals growing other assemblies with varying shapes. Rapid growth in the axial direction produces rope-like structures that can be made to form circles and loops through application of external forces. Other structures included egg shapes, disks, spirals, knots, and spheres.

Metal coordination is another important bonding opportunity with respect to self-assembly. This is important in many natural molecules such as hemoglobin and chlorophyll where the metal atom acts as both the site of activity and as a centralizing agent with respect to shape and thus acts as a nucleating agent for self-assembly.

There are many potential and real applications of self-assembly.

Pharmaceutical chiral drug sales top \$100 billion yearly worldwide. More than half of the drugs on the market are asymmetric molecules with about 90% administered as racemates. Generally, one optical center of a drug will have the desired activity while the other often produces negative side effects. Because of this the FDA, in 1992, issued a statement saying that for every new racemic drug, the two enantiomers must be treated as separate substances that are required to undergo pharmacokinetic and topological studies.

One direct approach to the separation of chiral compounds is called molecular imprint polymers that involves the formation of a three-dimensional cavity with the shape and electronic features that are complementary to the imprinted or target molecule.

11.7 TRANSFER AND RETENTION OF OXYGEN

Today the polymer scientist should be aware of synthetic, inorganic, and biological macromolecules. The field of biological macromolecules is large and is one of the most rapidly expanding areas of knowledge. It involves gene splicing and other related biological aspects including biological engineering, neurobiology, medicine, and drugs and the very elements of life and death, of thought and caution, of pain and health, of biological transference, and of energy and

biological matter. The polymer scientist can learn from these advances but must also contribute to their understanding on a molecular and chain aggregate level. The investigation of these biological macromolecules is done using state-of-the-art instrumentation and techniques and the use of scientific intuition. The world of the natural macromolecule is yielding information allowing an understanding on a molecular level. A striking example involves oxygen transfer and retention in mammals.

Oxygen retention and transfer involve the iron-containing organometallic planer porphyrin-containing structure called “heme” (Figure 11.1). The iron is bonded through classical coordination. The ferrous or iron(II) has six coordination sites. Four of these coordination sites are occupied by the nitrogen atoms of the four pyrrole-related rings of the porphyrin. A fifth site is occupied by one of the nitrogens of an imidazole side chain found as part of the protein structure and located just opposite the planer porphyrin moiety. The sixth site acts to bind oxygen. The iron remains in the +2 oxidation state, whether oxygen is being bound or the site is vacant. An additional histidine is present, residing in the protein chain opposite the sixth site of the iron atom. This second histidine does not bind iron but serves to stabilize the binding site for oxygen. Experimentally, heme does not bind oxygen. Instead, a complex protein wrapping is necessary to both assist binding and protect the binding site from foreign competitor molecules that could render the heme site inactive, either through structural change, change in iron oxidation state, or through occupation of this site, thus preventing oxygen access to the active binding site.

The precise electronic environment of iron deserves special comment. In deoxyhemoglobin, the iron atom has four unpaired electrons, but in oxyhemoglobin iron has no unpaired electrons. The iron in the oxygen-free deoxyhemoglobin is referred to as “high-spin” iron, whereas iron in oxyhemoglobin is called “low-spin” iron. Hund’s rule of maximum multiplicity calls for the most energy-favored, lowest energy form to be the structure containing the highest number of unpaired electrons. The binding of oxygen, itself with two unpaired electrons, is probably the result of a favored energy of binding brought about through the coupling of the two sets of unpaired electrons—the favorable energy allowing the violation of Hund’s rule.

There are two major protein-heme-binding macromolecules. These are myoglobin (Figure 11.2), which is used as an oxygen storage molecule in mammalian muscle, and hemoglobin, which is used in oxygen transport. *Myoglobin* is single stranded with one heme site per chain, whereas *hemoglobin* is composed of four protein chains, each one containing a single heme site (Figure 11.4). In hemoglobin, there are two sets of equivalent chains composing its quaternary structure. These two chain types are referred to as α and β chains. The α chains contain 141 amino acid units and the β chains contain 146 units. The myoglobin contains 153 amino acid units. Each of these chains is similar, and each forms the necessary environment to allow the heme site to bind oxygen

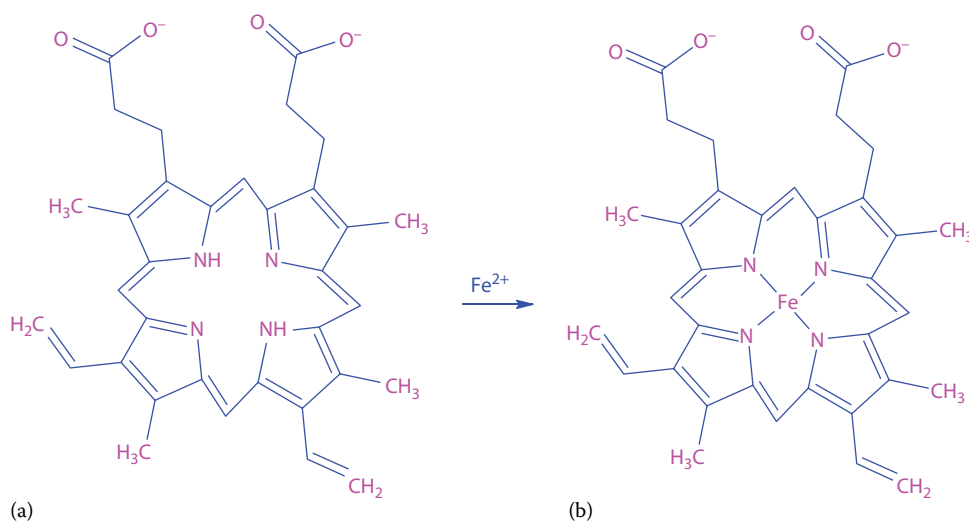


FIGURE 11.1 Porphyrin structures that serve as the basis of heme (a). Upon addition of iron, this porphyrin, which is called protoporphyrin IX, forms the heme group (b).

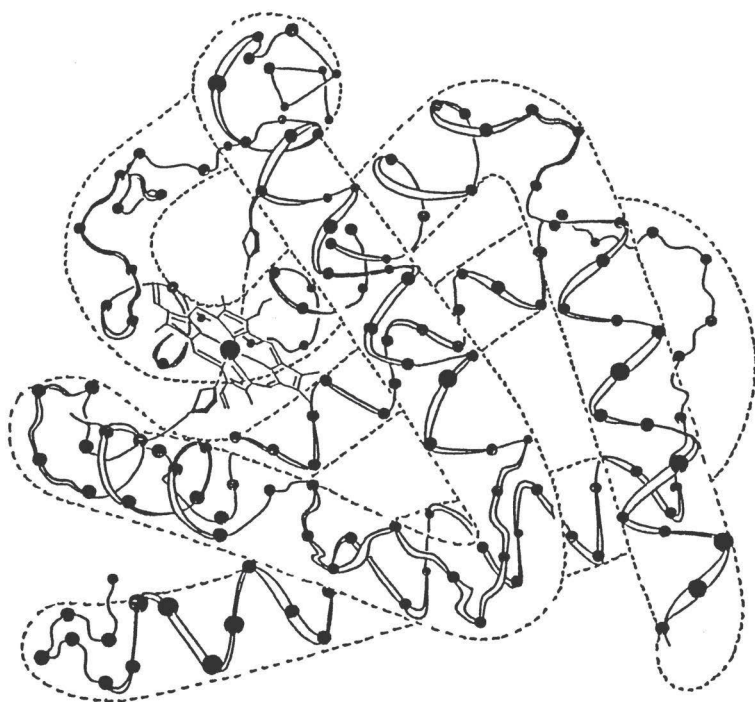


FIGURE 11.2 Generalized myoglobin structure showing some amino acid units as open circles to illustrate the *folded* tertiary structure.

in a reversible manner. The protein segments are described as being loosely helical with about 60%–80% of the structure helical.

While the chains are similar in overall structure, there exist somewhat subtle differences. For instance, the quaternary structure of hemoglobin permits interaction between the four chains. Structural movement brought about through binding of oxygen at one of the four heme sites acts to make it easier for subsequent oxygen addition at the other heme sites. Such cooperative binding of oxygen is not possible in the single-chained myoglobin. The consequence of this cooperative binding is clearly seen in a comparison of oxygen binding by both myoglobin and hemoglobin as a function of oxygen pressure (Figure 11.3). Oxygen binding occurs by myoglobin at even low oxygen pressures. This is referred to as hyperbolic behavior. By comparison, hemoglobin binding

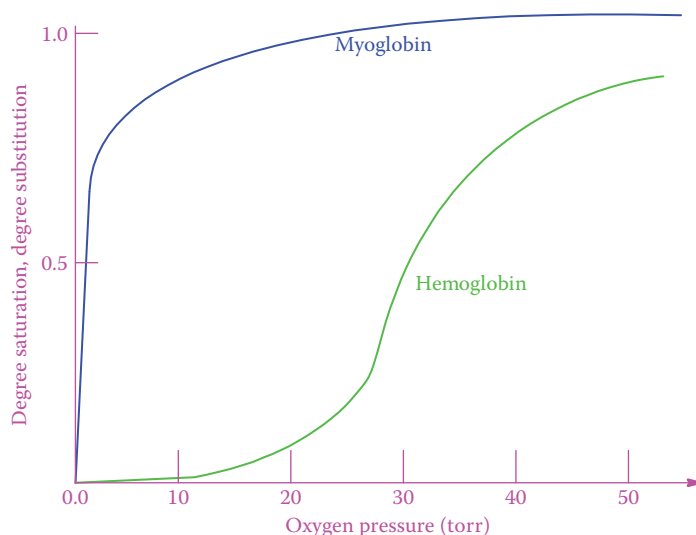


FIGURE 11.3 Degree of saturation as a function of oxygen pressure.

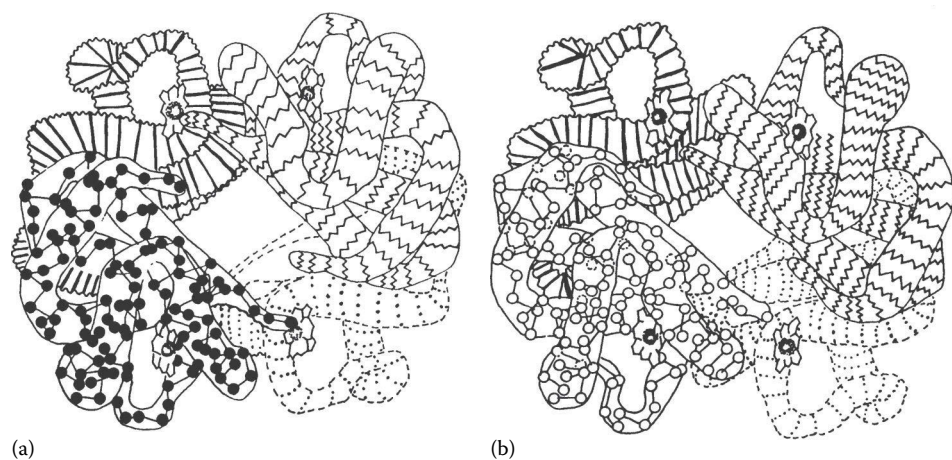
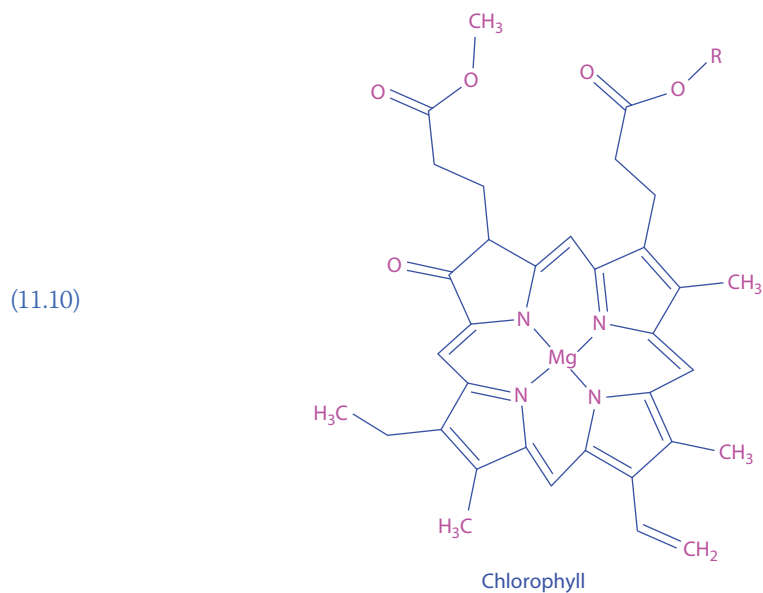


FIGURE 11.4 Space-filling models of deoxyhemoglobin (a) and oxyhemoglobin (b). Notice the small shifts in the overall geometry of the various protein chains and the decreased size of the inner core.

increases more slowly as the oxygen pressure increases, occurring in a more sigmoidal fashion. Thus, initial binding of oxygen at a heme site is relatively difficult, becoming increasingly easier as the number of heme sites bonded increases.

The differences in oxygen binding characteristics are related to the differing roles of hemoglobin and myoglobin. Thus, myoglobin is employed for the storage of oxygen in muscle. Binding must occur even at low oxygen contents. Hemoglobin is used for the transport of oxygen and becomes saturated only at higher oxygen concentrations. The oxygen content in the alveoli portion of our lungs is on the order of 100 torr (1 atm of pressure = 760 torr). Here, almost total saturation of the heme binding sites in hemoglobin occurs. By comparison, the oxygen level in the capillaries of active muscles is on the order of only 20 torr, allowing the hemoglobin to deliver about 75% of its oxygen and for myoglobin to almost reach saturation in oxygen binding.

Conformational changes accompany the binding and release of oxygen. These changes are clearly seen by superimposing the oxygen-containing form of hemoglobin (oxyhemoglobin) over the nonoxygen-containing form of hemoglobin (deoxyhemoglobin) (Figure 11.4). It is interesting to note that most enzymes have their active sites on the surface but enzymes, such as myoglobin, that are dealing with small molecules, such as oxygen, have their active sites hidden away in the internal portion so that other unwanted molecules cannot easily access them with the protein tunnel acting to restrain unwanted suitors:



Another metal-containing important enzyme, chlorophyll (11.10), is structurally related to myoglobin, and it is responsible for photosynthesis, the conversion of water and carbon dioxide, with the aid of solar energy, to carbohydrates.

11.8 NATURE'S MACROMOLECULAR CATALYSTS

Probably the most important reactions occurring on polymers involve the catalytic activity of a class of proteins called “enzymes.” The catalytic action is a result of a lowering of the activation energy for the rate-determining step in the reaction. In general terms, the catalytic action results from the formation of a complex between the enzyme and the molecule undergoing reaction. The decreased activation energy is a result of the reacting molecules being held by the enzyme in such a manner as to favor the appropriate reaction occurring. The two classical models employed to describe the formation of the complex between the reacting molecule(s) and the enzyme are the lock-and-key model and the induced-fit model. Briefly, the *lock-and-key model* calls for an exact or highly similar complementary fit between the enzyme and the reacting molecule(s) (Figure 11.5). Geometry plays an essential role in permitting the electronic (polar, electrostatic, etc.; attractions/repulsions) interactions to form the necessary complex with the correct geometry. Release is encouraged by the new geometry and electronic distribution of the resulting products of the reaction being sufficiently dissimilar. The *induced-fit model* is similar except that the enzyme originally does not fit the required shape (geometrical and electronic cavity). The required shape is achieved upon binding—the binding causing needed assisting factors or proximity and orientation to effect a decrease in the energy of the transition state. Figure 11.5 shows

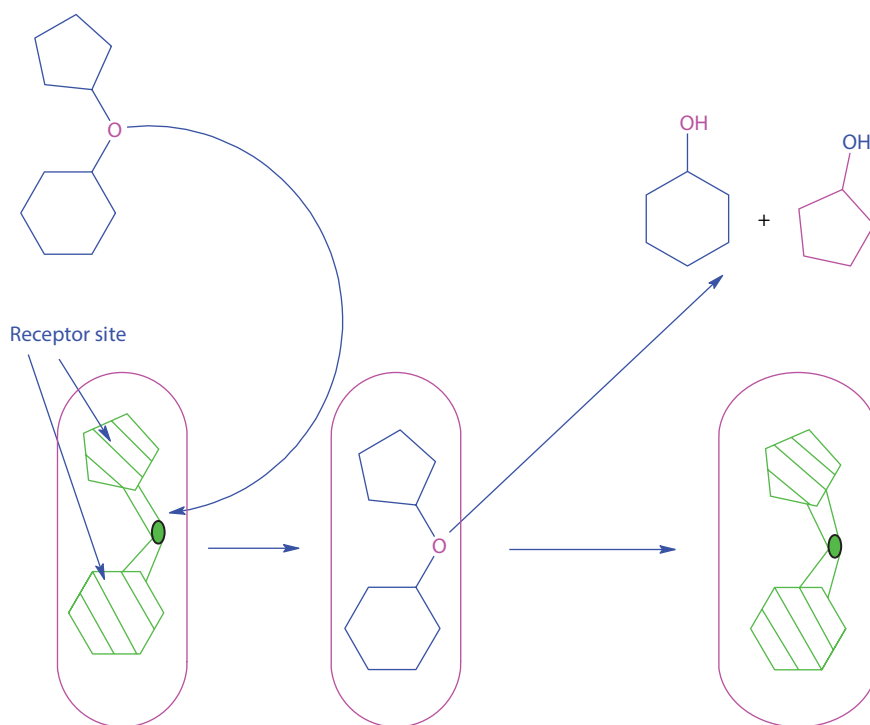


FIGURE 11.5 There are two major models for the binding of reactant molecules to the active sites of nonallosteric enzymes. This sequence describes the essential steps in the lock-and-key model, where the reactant(s) is attracted to the active site on the enzyme where the active site is a cavity of the same general size, shape, and (complementary) electronic features. Binding occurs and the appropriate reaction(s) occurs resulting in a change in the geometry and electronic configuration of the product, causing its release. The second model (not shown) is the induced-fit model where the individual steps are similar to the lock-and-key except the reactants *induce* a change in the conformation of the active site on the enzyme, allowing it to accept the reactant(s).

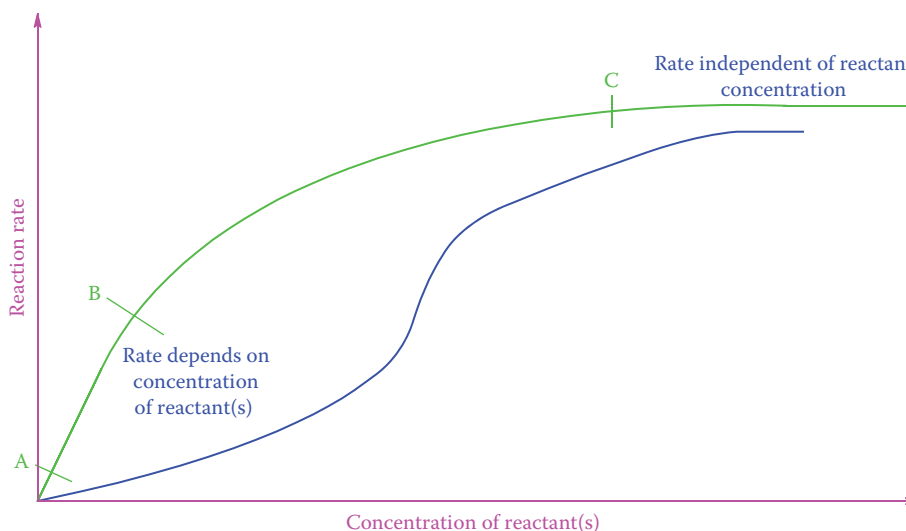


FIGURE 11.6 Dependence of reaction showing sigmoidal (bottom) and hyperbolic (top behavior). The top plot also shows the initial rate of reaction as a function of reactant concentration when the concentration of enzyme remains constant. The initial reaction rate, A to B, varies until the number of reactants clearly outnumbers the number of reaction sites on the enzyme, at which time, C, the rate becomes zero order, independent of the reactant concentration.

how the enzyme sucrase breaks sucrose into its basic units of glucose and fructose. The sucrose is held by the enzyme in such a fashion so that water easily and efficiently breaks the ether bond forming two hydroxyl units that are released because they no longer have the required shape/size/electronic features of the enzyme cavity.

Enzyme reactions generally follow one of two kinetic behaviors. Briefly, the oxygen binding curve for myoglobin is hyperbolic, whereas that for hemoglobin it is sigmoidal (Figure 11.6). In general, it is found that similar enzymes such as myoglobin follow a similar hyperbolic relationship between reaction extent and reaction time. More complex enzymes such as hemoglobin follow a sigmoidal relationship between reaction extent and reaction time. The primary difference involves the ability of different portions of the overall hemoglobin structure, removed reaction sites, to affect each other. Molecules in which various removed sites affect the reactivity of other removed sites are called “*allosteric enzymes*.”

The *Michaelis–Menten model* is commonly employed in describing *nonallosteric enzyme* reactions. The overall model can be pictured as follows (11.11) where E represents the enzyme, M the reacting molecule(s), $E + M \rightarrow EM$ is associated with k_1 , and the reverse reaction associated with k_{-1} and $EM \rightarrow E + P$ associated with k_2 :



Here, EM represents the enzyme complex and P the product(s). The rate of complex formation is described as

$$(11.12) \quad \text{Rate of complex formation} = \frac{d[EM]}{dt} = k_1[E][M]$$

The complex then either returns to form the initial reactants or forms the product(s) and the free enzyme, E. In kinetic terms, the change or rate of breakdown of the complex is described as

$$(11.13) \quad \text{Rate of complex change} = -\frac{d[EM]}{dt} = k_{-1}[EM] + k_2[EM]$$

The negative sign associated with the equation means that the terms are describing the rate of decrease in complex concentration. The rate of complex formation is rapid, and fairly soon the rate at which the complex is formed is equal to the rate at which it breaks down. This situation is called a steady state. Mathematically, this is described by

$$(11.14) \quad \frac{d[EM]}{dt} = -\frac{d[EM]}{dt}$$

and

$$(11.15) \quad k_1[E][M] = k_{-1}[EM] + k_2[EM]$$

Often it is difficult to directly measure the concentration of E as the reaction progresses. Thus, the concentration of E is generally dealt with using an approach as shown in Equations 11.16 through 11.25:

$$(11.16) \quad [E] = [E_0] - [EM]$$

where $[E_0]$ is the initial enzyme concentration.

Substitution of this description for $[E]$ into Equation 11.12 gives

$$(11.17) \quad k_1 ([E_0][M] - [EM][M]) = k_{-1}[EM] + k_2[EM]$$

Separating out $[EM]$ on the right-hand side gives

$$(11.18) \quad k_1 ([E_0][M] - [EM][M]) = (k_{-1} + k_2)[EM]$$

Bringing together all of the rate constants from both sides of the equation gives

$$(11.19) \quad [E_0][M] - [EM][M] = k'[EM]$$

Moving the $[EM]$ containing terms to the right side gives

$$(11.20) \quad [E_0][M] = k'[EM] + [EM][M]$$

and separating out $[EM]$ from the right side gives

$$(11.21) \quad [E_0][M] = [EM] (k' + [M])$$

Now division of both sides by $k' + [M]$ gives

$$(11.22) \quad [EM] = \frac{[E_0][M]}{k' + [M]}$$

The initial rate of product formation, R_i , for the Michaelis–Menten model depends only on the rate of complex breakdown, that is,

$$(11.23) \quad R_i = k_2[EM]$$

Substitution from Equation 11.21 into Equation 11.22 gives

$$(11.24) \quad R_i = \frac{k_2[E_0][M]}{k' + [M]}$$

This expression is dependent on the concentration of M and describes the initial part of the plot given in Figure 11.6.

Generally, the concentration of M far exceeds that of the enzyme sites such that essentially all of the enzyme sites are complexed, that is, $[EM] = [E_0]$. (This is similar to a situation that occurs regularly in South Florida where four- and six-lane roads are funneled into a two-lane section of road because of a wreck or road construction.) Thus, the rate of product formation is maximized under these conditions. This maximum rate, R_m , allows us to substitute $[E_0]$ for $[EM]$ in Equation 11.23 to give

$$(11.25) \quad R_m = k_2[E_0]$$

Since the enzyme concentration is constant, the rate of product formation under these conditions is independent of $[M]$ and is said to be zero order (Figure 11.6).

The maximum rate is directly related to the rate at which the enzyme *processes* or permits conversion of the reactant molecule(s). The number of moles of reactants processed per mole of enzyme per second is called the “**turnover number**.” Turnover numbers vary widely. Some are high, such as for the scavenging of harmful free radicals by catalase, with a turnover number of about 40 million. Others are small such as the hydrolysis of bacterial cell walls by the enzyme lysozyme, with a turnover number of about one-half.

The Michaelis–Menten approach does not describe the behavior of allosteric enzymes, such as hemoglobin, where rate curves are sigmoidal rather than hyperbolic. A more complex mode is called for to account for the biofeedback that occurs with allosteric enzymes. Such affects may be positive such as those associated with hemoglobin, where binding by one site changes the geometry and electronic environment of the other remaining sites, allowing these additional sites to bind oxygen under more favorable conditions. The effects may also be negative. For instance, cytidine triphosphate inhibits ATCase and catalyzes the condensation of aspartate and carbamoyl phosphate—forming carbamoyl aspartate.

Two major models are typically used to describe these situations: the concerted model and the sequential model. In the *concerted model*, the enzyme has two major conformations—a relaxed form that can bind the appropriate reactant molecule(s) and a tight form that is unable to tightly bind the reactant molecule(s). In this model, all subunits containing reactive sites change at the same time (Figure 11.7). An equilibrium exists between the active and inactive structures. Binding at one of the sites shifts the equilibrium to favor the active relaxed form.

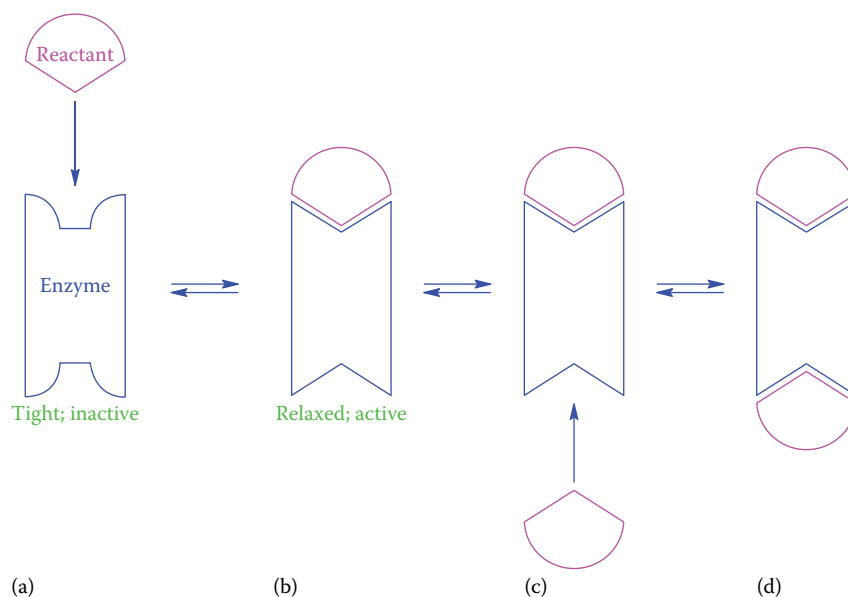


FIGURE 11.7 Concerted model for allosteric enzymes. The major steps are (a) and (b). An equilibrium exists between the tight (a) and relaxed (b) forms of the allosteric enzyme. The reactant molecule(s) approaches the reactive site of one of the enzyme sites present in the relaxed form (c). Binding occurs, shifting the equilibrium to the relaxed form(s). The second site is bound (d).

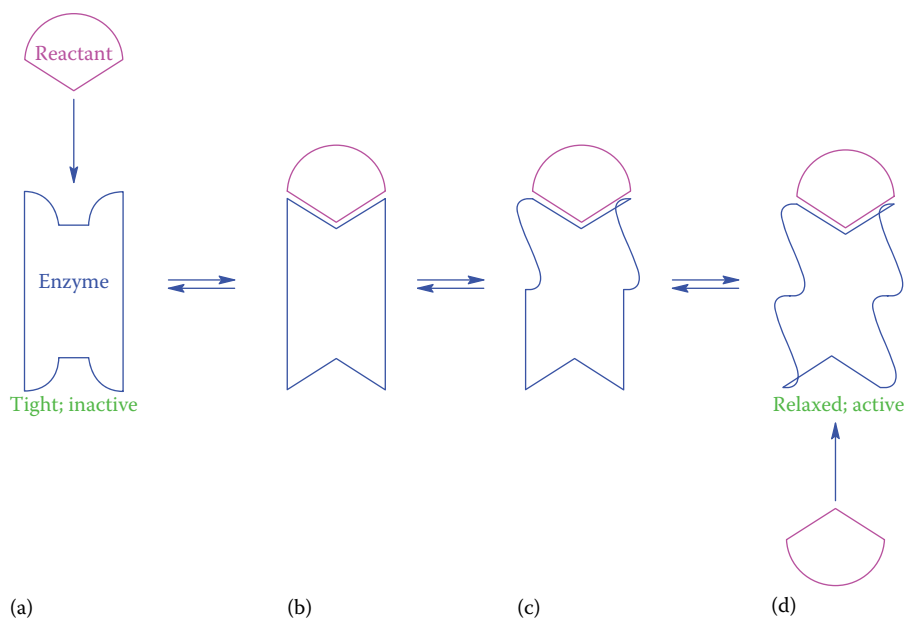


FIGURE 11.8 Sequential model for allosteric enzymes. The individual steps are as follows: the reactive molecule(s) approach the reactive site (a), which typically has a cavity similar to, but not the same as, the reactant molecule(s); a conformational change is effected so that the reactive molecule(s) can be bound (b); the bound portion of the enzyme changes shape; this shape change is transmitted to the other unit(s) containing active sites (c); the remaining enzyme portion containing active sites undergoes a conformational change that makes binding easier (d).

The major feature in the *sequential model* is the induction of a conformational change from the inactive tight form to the active relaxed form as the reacting molecule(s) is bound at one of the sites. This change from an unfavorable to a favorable structure is signaled to other potentially reactive sites bringing about a change to the more favored structural arrangement in these other sites (Figure 11.8).

Structural changes can be brought about through simple electrostatic and steric events caused by the presence of the reacting molecule(s). Structural changes also result as cross-linking and other primary bonding changes occur.

11.9 PHOTOSYNTHESIS

11.9.1 GENERAL

The recent environmental issues related to the green house effect and atmospheric contaminations heighten the importance of obtaining energy from clean sources such as photosynthesis. Photosynthesis also acts as a model for the creation of synthetic light harvesting systems that somewhat mimic chlorophyll in their ability to convert sunlight into usable energy (Picture 11.1). The basis of natural photosynthesis was discovered by Melvin Calvin, one of my academic grandfathers. Using carbon 14 as a tracer, Calvin and his team found the pathway that carbon undergoes in a plant during photosynthesis. They showed that sunlight supplies the energy through the chlorophyll site allowing the synthesis of carbon-containing units, saccharides or carbohydrates. Chlorophyll (Structure 11.10) has a metal embedded in a polymer matrix and illustrates the importance of metals in the field of photochemistry and photophysics. The following is a description of that activity of chlorophyll in creating energy from the sun.

The maximum solar power density on Earth is approximately 1350 W/m^2 . When it enters the Earth's atmosphere, it drops approximately to 1000 W/m^2 due to absorption in the atmosphere. The amount of light energy used in photosynthesis is immense, about 100 TW yearly



PICTURE 11.1 Essentially all plant life depends on chlorophyll to assist in photosynthesis and give plants the green color.

or about seven times the yearly human consumption. Here, organisms convert about 10^{11} tons of carbon into biomass yearly.

Solar energy is a clean and economical energy source, but it must be converted into useful forms of energy. For example, solar energy can be used as a source of excitation to induce a variety of chemical reactions.

Plants and algae are natural examples of the conversion of light energy, and this energy is used to synthesize organic sugar-type compounds through photosynthesis. This process has a great importance for survival of all life on our planet because it provides the energy and reduces the carbon dioxide as well as produces molecular oxygen necessary for oxygen-consuming organisms. In fact, this process can be considered as a vital link between material and energy recycling in the biosphere.

In photosynthesis, green plants and some bacteria harvest the light coming from the sun by means of their photosynthetic antenna systems. The light harvesting starts with light gathering by antenna systems, which consist of pigment molecules including chlorophylls, carotenoids, and their derivatives. The absorbed photons are used to generate excitons, which then travels via energy transfers toward the reaction centers (RCs). This overall series of processes is represented in Figure 11.9. The series can be remembered by the initials “ARC” where A represents antenna pigments, R represents the RCs, and C represents chlorophylls and carbohydrates.

In RCs, the energy is used as a driving force for an electron transfer reaction, which in turn initiates a series of slower chemical reactions, and the energy is saved as redox energy inducing a charge separation in a chlorophyll dimer called the special pair $(\text{chlorophyll})_2$. Charge separation, which forms the basis for photosynthetic energy transfer, is achieved inside the RCs:



FIGURE 11.9 Light is absorbed by the antenna pigments, A, transferring the energy until it reaches the reaction center, R, where it is used as the driving force for electron transfer reactions where specialized chlorophylls use it to form carbohydrates.

Specialized RC proteins are the final destination for the energy where it is converted into chemical energy by means of electron transfer reactions. These proteins consist of a mixture of polypeptides, chlorophylls (plus the special pair), and other redox-active cofactors. In the RCs, a series of downhill electron transfers occur resulting in the formation of a charge-separated state. Based on the nature of the electron acceptors, two types of RCs can be described. For the first type (photosystem I), the RC contains iron–sulfur clusters (Fe_4S_4) as their electron acceptors and relays, whereas the second type (photosystem II) features quinones as their electron acceptors. Both types of RCs are present in plants, algae, and cyanobacteria, whereas the purple photosynthetic bacteria have only a photosystem II and the green sulfur bacteria contain a photosystem I. To gain a better understanding of these two types of RCs, each will be further discussed.

11.9.2 PURPLE PHOTOSYNTHETIC BACTERIA

In the mid-1980s, Deisenhofer reported his model for the structure of photosystem II for two species of purple photosynthetic bacteria (*Rhodospseudomonas viridis* and *Rhodobacter*) based on x-ray crystallography of the light harvesting device II. Photosynthetic centers in purple bacteria are similar, but not exactly, examples for the green plants but they are simpler and better understood so will be described here. The photosynthetic membrane of purple photosynthetic bacteria is composed of many phospholipid-filled ring systems (LH II) and several larger dissymmetric rings (LH I) stacked almost like a honey comb. Inside the LH I is a protein called the RC as illustrated in Figure 11.10.

The light harvesting antenna complex LH II is composed of two rings of bacteriochlorophylls *a* (BChl) molecules that can be classified into two categories. The first one is a set of 18 molecules arranged in a slipped face-to-face arrangement and is located close to the membrane surface perpendicularly to these molecules. The second ring is composed of 9 BChl in the middle of the bilayer. The first 18 BChl has an absorption maximum at 850 nm and are called B850, while the second (9 BChl) have absorption maximum at 800 nm and are called B800. These structures are contained within the walls of protein cylinders with radii of 1.8 and 3.4 nm. Once the LH II complex antenna absorbs light, a series of very complex nonradiative photophysical processes are triggered. First, the excitation energy migrates via energy transfers involving the hopping of excitation energy within almost isoenergetic subunits of a single complex, which is then followed by fast energy transfer to a lower energy complex with minimal losses (Figure 11.11). These ultrafast events occur in the singlet state (S_1) of the BChl pigments and are believed to occur over relatively long distances (30–100 Å).

The energy collected by the LH II antenna is transferred to another antenna complex known as LH I, which surrounds the RC. The photosynthetic RCs of bacteria consist mainly of a protein, which is embedded in and spans a lipid bilayer membrane. In the RC, a series of electron transfer reactions are driven by the captured solar energy. As a result of these electron transfer reactions, the captured solar energy is converted to chemical energy in the form of a charge

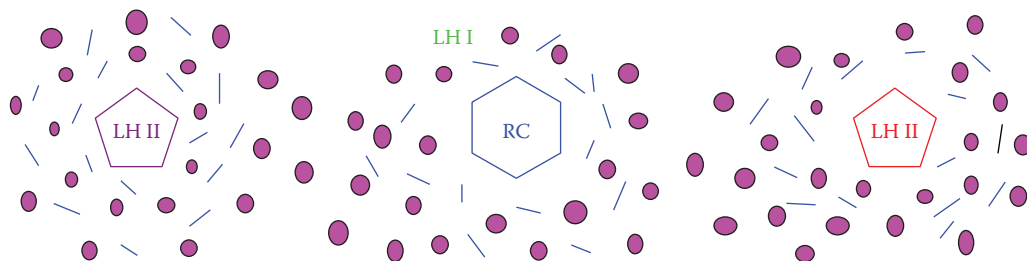


FIGURE 11.10 Simplified drawing showing two light harvesting II assemblies next to one light harvesting I unit. The circles are polypeptides and the lines represent rings of interacting bacteriochlorophylls *a* (called B850). In the middle of LH I, there is a protein called the reaction center where the primary photoinduced electron transfer takes place from the special pair of bacteriochlorophylls *b*.

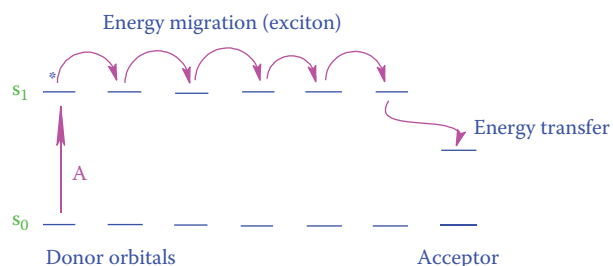


FIGURE 11.11 The exciton and energy transfer processes.

separation process across the bilayer. The photosynthetic RC is where the harvested solar energy is converted to chemical energy via charge separation across the bilayer by means of an electron transfer reaction.

A special pair of BChl (P870) is excited from either the absorption of a photon or by acquiring this excitation energy from an energy transfer from the peripheral antenna BChl (not shown for simplicity) triggering a photoinduced electron transfer inside the RC. Two photoinduced electrons are transferred to a plastoquinone placed inside the photosynthesis membrane acting as an electron acceptor and is consequently reduced to a semiquinone and finally to a hydroquinone. This reduction involves the uptake of two protons from water on the internal cytoplasmic side of the membrane. The formed hydroquinone then diffuses to the next component of the apparatus, a proton pump called the cytochrome bc1 complex.

The next step involves the oxidation of the hydroquinone back to a quinone and the energy released being used for the translocation of the protons across the membrane thus establishing a proton concentration and charge imbalance (proton motive force). Thus, the oxidation process takes place via a series of redox reactions triggered by the oxidized special pair, which at the end is reduced to its initial state. The oxidation process is ultimately driven, via various cytochrome redox relays, by the oxidized P870, which becomes reduced to its initial state. Finally, the enzyme ATP synthase allows protons to flow back down across the membrane driven by the thermodynamic gradient, leading to the release of ATP formed from adenosine diphosphate and inorganic phosphate (Pi). The ATP fills the majority of the energy needs of the bacterium.

11.9.3 GREEN SULFUR BACTERIA

The observation of a photosynthetic RC in green sulfur bacteria dates back to 1963. Green sulfur bacteria RCs are of the type I or the Fe-S-type (photosystem I) where the electron acceptor is not the quinone, but instead chlorophyll molecules (BChl 663, 8¹-OH-Chl *a*, or Chl *a*) serving as primary electron acceptors and three Fe₄S₄ centers (ferredoxins) as secondary acceptors. A quinone molecule may or may not serve as an intermediate carrier between primary electron acceptor (Chl) and secondary acceptor (Fe-S centers).

A large number of chlorophyll antennas are used to harvest the solar energy, which in turn are used to excite the special pair P₇₀₀. The P₇₀₀ donor will in turn transfer an electron to a primary acceptor (A₀, pheophytin) and in less than 100 ps to a secondary acceptor (A₁, a phylloquinone). The electron received by A₁ is in turn transferred to an iron–sulfur cluster and then to the terminal iron–sulfur acceptor.

11.10 MECHANISMS OF PHYSICAL ENERGY ABSORPTION

Let us consider a force, stress, acting on a material producing a deformation. The action of this force can be described in terms of two models—a Hookean spring and a Newtonian dashpot (Section 13.1). In the Hookean spring, the energy of deformation is stored in the spring and may be recovered by allowing the spring to act on another load or through release of the stress; in either case, the site is returned to zero strain. A Newtonian dashpot is pictorially a frictionless

piston and is used to describe chains flowing past one another. The energy of deformation is converted to heat. In actuality, the deformation of most plastics results in some combination of Hookean and Newtonian behavior. The Newtonian behavior results in net energy adsorption by the stressed material, some of this energy producing the work of moving chains in an irreversible manner while some of the energy is converted to heat.

There are three major mechanisms of energy absorption: shear yielding, crazing, and cracking. The latter two are often dealt with together and called “normal stress yielding.”

We can distinguish between a crack and a craze. When stresses are applied to polymeric materials, the initial deformation involves shear flow of the macromolecules past one another if it is above T_g , or bond bending, stretching, or breaking for glassy polymers. Eventually, a crack will begin to form, presumably at a microscopic flaw. This crack can then propagate at high speed, often causing catastrophic failure. The applied stress results in a realigning of the polymer chains. This results in greater order but decreased volume occupied by the polymer chains, that is, an increase in free volume. This unoccupied volume often acts as the site for opportunistic smaller molecules to attack, leading to cracking and crazing and eventually property failure.

A *crack* is an open fissure, whereas a *craze* is spanned top to bottom by fibrils that act to resist entrance of opportunistic molecules such as water vapor. Even here, some smaller molecular interactions can occur within the void space, and eventually the specimen is weakened.

Crazing and cracking can be induced by stress or combined stress and solvent action. Most typical polymers show similar features. To the naked eye, crazing and cracking appear to be a fine, microscopic network of cracks generally advancing in a direction at right angles to the maximum principle stress. Such stress yielding can occur at low stress levels under long-term loading. Suppression of stress yielding has been observed for some polymers by imposition of high pressure.

In shear yielding, oriented regions are formed at 45° angles to the stress. No void space is produced in shear yielding. Crazing often occurs prior to and in front of a crack tip. As noted before, the craze portion contains both fibrils and small voids that can be exploited after the stress is released or if the stress is maintained. Materials that are somewhat elastic are better at preventing small stress-related crazing and cracks. Most plastics are not ideal elastomers and additional microscopic voids occur each time a material is stressed.

All three mechanisms result in a difference in the optical properties of the polymeric material because of the preferential reorientation, with realignment of the polymer chains resulting in a change in optical properties such as refractive index, allowing detection through various optical methods including visual examination, microscopy, and infrared spectroscopy of films and sheets. Crazed and cracked sites of optically clear materials appear opaque, whereas shear-yielded sites may appear to be *wavy* when properly viewed by the naked eye employing refracted light.

It is important to emphasize that the surface layers of most polymeric materials are different from the bulk material and are often more susceptible to environmental attack. Thus, special surface treatments are often employed in an attempt to protect the surface molecules.

Directly related to energy absorption is energy dissipation. Generally, the better a material can dissipate or share applied energy the more apt it is to retain its needed properties subsequent to the applied energy. Polymers dissipate applied energies through a variety of mechanisms including rotational, vibrational, electronic, and translational modes.

One area that illustrates aspects important to energy dissipation is the fabrication of protective armor. Such armor includes helmets, vests (Picture 11.2), vehicle exteriors and interiors, riot shields, bomb blankets, explosive containment boxes (aircraft cargo), and bus and taxi shields. In each case energy dissipation is a critical element in the desired behavior of the device. To illustrate this let us look at body armor.

Most of the so-called bulletproof vests were made of PC. More recently, layers of PE were found to have similar *stopping power* for a lesser weight of material.

Today, most body armor is a complex of polymeric materials. Rapid dissipation of energy is critical, allowing the impact energy to be spread into a wide area. Materials should be strong enough so as not to immediately break when impacted and that they need to have enough contact with other parts of the body armor to allow ready transfer of some of the impact energy. If the material can adsorb some of the energy through bond breakage or heating, then additional energy can be absorbed at the site of impact. Along with high strength, the material should have



PICTURE 11.2 Bullet-resistant vest used by police, armed services personnel, and other persons for protection.

some ability to stretch and to move allowing the material to transfer some of the energy to surrounding material. If the connective forces between the components are too strong, total energy dissipation is reduced because a strong bond discourages another way of reducing the impact energy, that is, allowing the various materials to slide past one another. Thus, a balance is needed between material strength, strength of bonding holding the components together, and the ability to readily dissipate the impact energy.

Recently, it was found that some sequences of layered materials are more effective at energy dissipation than others. One of the better combinations is obtained when aramid layers are adjacent to ultrahigh molecular weight linear polyethylene (UHMWPE).

Another factor is breaking up the projectile. This is again done using polymeric materials—here composites such as boron carbide ceramics in combination with aramids, UHMWPE, or fibrous glass.

One of the most recent approaches employed to increase the effectiveness of body armor involves the use of *shear thickening fluids* (STFs). These combinations are generally referred to as “liquid armor.” As force is inflected to an STF, it resists flow different to many liquids such as water. STF material is placed between the Kevlar sheets that perform several functions. Because it is a liquid under normal conditions, it adds to the flexibility of the body armor. Second, it is more effective at preventing penetration of a bullet so it allows less material to be used to achieve the same *stopping power*, allowing the armor to weigh less. Finally, it helps blunt the projectile through its action as an STF. Most STFs are polymeric. The liquid is generally low-molecular-weight poly(ethylene glycol) (PEG) with silica particles dispersed in it. The PEG wets the Kevlar sheets assisting the Kevlar–STF combination to spread the impact dissipating the effect of the projectile.

11.11 BREAKAGE OF POLYMERIC MATERIALS

When a plastic is broken by a sharp blow or cut, are polymer chains broken? The important factors include the nature of the polymer, chain length, and arrangement of the chains.

Sperling and coworkers looked at the question of how many chains are broken and the defining factors related to this breakage when a polymeric material is cut or broken. They used various chain lengths of PS and employed a dental drill as the cutting implement.

Pictorially, the problem can be described as looking at a robin pulling a worm out of a hole. Does the robin get the entire worm or some fraction of the worm? The factors are similar and deal with the length of the worm and how far into the hole it is. If it is largely within the hole, then it can grasp the dirt, roots, etc., about it to *hold on for dear life*. If not, then the worm is a meal for the *early bird*.

It turns out that the question dealt with here is related to determining the critical length of fibers that are to be used in a composite. When determining the optimum fiber length of a fiber in a matrix, measurements are made using fibers of differing lengths. If a fiber can be removed from the matrix unbroken, then it is too short, and if the fiber breaks before it can be removed, then the fiber is too long. Thus, fiber lengths should be such that the fiber just begins to be broken rather than allowing it to be removed intact. In a composite, the worm is the fiber and the soil is the matrix. For the plastic, the worm is the individual chain and the soil is the remainder of the plastic. For the composite, the fiber contains many individual polymer chains, while for the situation dealt with here, individual polymer chains will be examined.

The length of fiber or chain that can be removed without breaking is related to the frictional and attractive energies between the fiber and the matrix or other polymer chains holding onto the chain. Thus, if the strength holding together the polymer backbone is greater than the frictional energy holding the chain in place, then the polymer chain will be removed unbroken. In general, what was found through calculations was that PS chains to 300 units in length are capable of being removed intact without breakage. This is in rough agreement with what Sperling found experimentally. Thus, individual PS chains up to about 300 units in length are removed from the plastic without chain breakage.

The relationship between chain length and chain breakage was found to be directly related to the typical length of chain necessary to produce physical cross-links, that is, chain entanglements (Figure 11.12). (This is probably due to the fact that chain entanglements greatly increase the *apparent* chain length and frictional energy needed to be overcome to move a chain.) Typically, at least one chain entanglement is needed to guarantee some chain breakage. For many vinyl polymers, including PS, one chain entanglement occurs for every 300 units. Experimentally, it was found that as the length of the PS chain increases so does the number of chain entanglements so that with a chain length of about 2000 (or an average of 7 chain entanglements), 50% of the chains are broken and when the chain length is about 4000 (or an average of 13 entanglements), approximately 100% of the chains break.

The production of chain entanglements is statically directly related to polymer length for linear chains, and almost independent of the nature of the vinyl unit for many polymers.

Chain length and entanglement are also related to the strength of the polymeric material. As chain length increases, the number of entanglements increases as does strength. At about eight entanglements, the relationship between the number of entanglements (and chain length) and

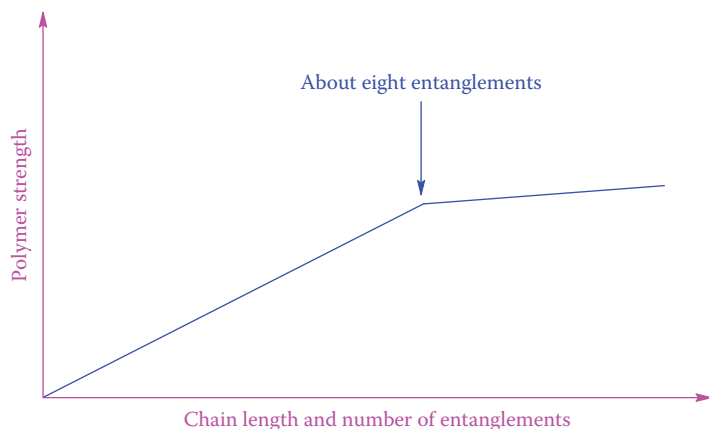


FIGURE 11.12 Idealized relationship between chain length and number of entanglements and polymer strength.

the polymer strength levels off with only small changes in polymer strength occurring as the chain length and the number of entanglements further increases as shown in Figure 11.12.

Because the distance between each entanglement is about 300 units and to achieve nearly maximum strength, eight entanglements are needed and a chain of about 2400 (300 units/entanglement \times 8 entanglements) units is needed. Calculations relating chain strength (related to the energy necessary to break a chain) and frictional force to hold a chain of varying length in place, that is,

$$(11.27) \quad \text{Chain strength} \propto \text{Frictional force as a function of chain length}$$

have been carried out with chain lengths of about 2000–3000 required before the frictional force necessary to break the chain occurs. This is in rough agreement with the chain length of 2400 calculated earlier using chain entanglement as the limiting factor.

As the polymer chain length increases, so does the viscosity of the melted polymer requiring more energy to process the polymers using any technique that requires the polymer to flow. This includes most of the molding processing typically used to process vinyl polymers. For many applications, the maximum strength is not needed so that industry looks to a balance between chain length and necessary strength. This *balance* is often chosen such that the chain length is sufficient to give seven entanglements rather than the eight required to insure about 100% chain breakage and maximum polymer strength, as noted earlier.

There are exceptions to this. One exception involves UHMWPE, which has few chain entanglements so it is easier to pull long chains from a PE matrix without chain breakage. The equivalent energy necessary to pull a UHMWPE chain from a PE matrix occurs at about a chain length of 100,000 (or a DP of about 3,300), much larger than that for PS.

For condensation polymers, the attractive forces between chains and chain units is greater so that physical chain entanglement is not necessarily the limiting factor, but rather other factors including localized crystallization become important.

SUMMARY

1. Polymers undergo reactions that are analogous to smaller molecules. Variation generally involves the need for reactants to have contact with the active site. This is more difficult for polymers.
2. Polymer degradation typically occurs via random chain scission, depolymerization, or both, resulting in a loss of chain length and properties associated with polymer length.
3. Among the most important reactions on polymers are those that occur with biomacromolecules such as involved in the transfer of oxygen and the activity of enzymes. Shape, size, and electronic configuration are all essential factors in the transfer of oxygen and activity of enzymes. The transfer of oxygen can be mathematically described using the classical Michaelis–Menten approach. The two major models describing the activity of nonallosteric enzymes such as myoglobin are referred to as the lock-and-key model and the induced-fit model. Hemoglobin is an example of an allosteric enzyme where the two most popular models describing this behavior are the concerted and sequential models.

GLOSSARY

Anchimeric reactions: Reactions enhanced by the presence of a neighboring group.

Chain scission: Breaking of a polymer chain.

Curing: Cross-linking producing a polymer network.

Cyclized rubber: Isomerized rubber containing cyclohexane rings.

Heme: Iron-containing active site for hemoglobin and myoglobin.

Hemoglobin: Allosteric enzyme responsible for the transport of oxygen in our bodies; contains four myoglobin-like units.

Hydrogenation: Addition of hydrogen to an unsaturated compound.

Induced-fit model: One of two basic models employed to describe enzymatic behavior of non-allosteric molecules. Here, the steps are similar to the lock-and-key model except the reactants *induce* a change in the conformation of the active site allowing the active site to bind with the reactant.

Kraton: Trade name for ABA block copolymer of styrene (A) and butadiene (B).

Kuhn element: Number of repeat units needed so that the most probable distance between the first and the growing end is back at the first unit again.

Ladder polymer: Double-stranded polymer for added stability.

Lock-and-key model: One of the two basic models to describe the selectivity and catalytic nature of nonallosteric enzymes. In this model the reactant(s) is attracted to the active site on the enzyme, which is of the same general size, shape, and complementary electronic nature as the reactant.

Macromolecular monomers (macromers): Polymers containing one reactive end group.

Myoglobin: Nonallosteric enzyme responsible for the storage of oxygen in our bodies. The activity follows the kinetic scheme described by Michaelis–Menten.

Ozonolysis: Reaction of an unsaturated organic compound with ozone.

Photosynthesis: Metabolic pathway for the conversion of carbon dioxide into organic compounds, mainly carbohydrates, using sunlight as the energy source.

RIM: Reaction injection molding.

Telechelic polymers: Polymers containing two active ends.

Telomerization: Abstraction of an atom by a macroradical.

Topochemical reactions: Reactions on the surface.

Williamson reaction: Reaction of an alkoxide and an alkyl chloride.

EXERCISES

1. In general, which metal ions are better chelated by polymers such as the salt of poly(acrylic acid)?
2. What is the general mechanism for the curing of step-reaction polymers?
3. Write the formula for perdeuterated polyethylene.
4. What is the major difference between reactions occurring on benzene and polystyrene.
5. When would you expect a polymer to undergo degradation via random scission?
6. How might you cross-link a polyethylene coating after it is applied to a wire?
7. How might you prepare a block copolymer of styrene and an alternating copolymer of ethylene and propylene?
8. What is the similarity between completely hydrogenated *Hevea brasiliensis* and completely hydrogenated gutta-percha?
9. What part does the porphyrin play in transmitting oxygen?
10. Would you expect polypropylene chains with a DP of 200 to break when a PP plastic is broken into two pieces?
11. What are the most important structural factors involved in natural catalysis?
12. What product would be produced from the ozonolysis of polybutadiene?
13. Write the structural formula for the polymeric hydrolytic products from (a) poly(vinyl acetate) and (b) poly(methyl methacrylate).
14. Why is commercial methylcellulose more soluble in water than native cellulose?
15. Why is CMC used in detergent formulations?
16. Would you expect the addition of chlorine or hydrogen to a double bond in a polymer to occur 100%?
17. What is the DS of cellulose nitrate when it is used as an explosive?
18. Why is the DS of cellulose triacetate only 2.8 and not 3.0?
19. Which is more polar: (a) cellulose triacetate or (b) cellulose diacetate?
20. Why is poly(vinyl butyral) not 100% vinyl butyral units?
21. If you have poly(vinyl alcohol) and you want to make it less hydrophilic using a condensation reaction, what might you use?
22. What products would you expect from the combustion of most vinyl polymers.

23. What monomer would be obtained by the decomposition of PVA?
24. Which would be more resistant to nitric acid: (a) polystyrene or (b) perfluoropolystyrene?
25. What ions would be removed from water by sulfonated polystyrene: (a) cations or (b) anions?
26. What reaction occurs when tannic acid is added to proteins such as those present in cowhide?
27. Which of the following should be most susceptible to degradation by acids and bases: (a) PS, (b) PVC, (c) PET, (d) nylon 66, (e) proteins, or (f) DNA?
28. Propose a procedure for recovering monomeric methyl methacrylate from scrap PMMA.
29. Why is PVC so thermally unstable?
30. Outline the three general steps in operation for photosynthesis.

FURTHER READING

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Testing and Spectrometric Characterization of Polymers

12

Public acceptance of polymers is usually associated with an assurance of quality based on knowledge of successful long-term and reliable testing. In contrast, much of the dissatisfaction with synthetic polymers is related to failures that might have been prevented by proper testing, design, and quality control. The American Society for Testing and Materials (ASTM), through its various committees, has developed many standard tests that may be referred to by all producers and consumers. There are also cooperating groups in many other technical societies such as the American National Standards Institute and the International Standards Organization (ISO), standard societies such as the British Standards Institution in England and Deutsche Normenausschuss in Germany, and comparable groups in every nation with developed polymer technology throughout the world.

Testing is done by industry to satisfy product specifications and for public protection using standardized tests for stress–strain relationships, flex life, tensile strength, etc. The U.S. tests are overseen by the ASTM through a committee arrangement. For instance, Committee D-1 oversees tests related to coatings while Committee D-20 oversees tests on plastics. New tests are continuously being developed, submitted to the appropriate ASTM committee, and, after adequate verification through *round robin* testing, finally accepted as standard tests. These tests are published by the ASTM. Each ASTM test is specified by a unique combination of letters and numbers, along with exacting specifications regarding data gathering, instrument design, and test conditions, making it possible for laboratories throughout the world to reproduce the test and hopefully the test results if requested to do so. The Izod test, a common impact test, has the ASTM number D256-56(1961). The latter number, 1961, is the year the test was first accepted. The ASTM publication gives instructions for the Izod test specifying test material shape and size, exact specifications for the test equipment, detailed description of the test procedure, and how results should be reported. Most tests developed by one testing society have analogous tests or more often utilize the same tests so that they may have ASTM, ISO, and other standardized society identification symbols.

A number of physical tests emphasizing stress–strain behavior will be covered in Chapter 13. Here we will concentrate on other areas of testing, emphasizing thermal and electrical properties, and on the characterization of polymers by spectral means. Spectroscopic characterization generally concentrates on the structural identification of materials. Most of these techniques, and those given in Chapter 13, can also be directly applied to nonpolymeric materials such as small organic molecules, inorganic compounds, and metals.

The testing of materials can be based on whether the tested material is chemically changed or is left unchanged. Nondestructive tests are those that result in no chemical change in the material, which may include many electrical property determinations, most spectroanalyses, simple phase change tests (T_g and T_m), density, color, and most mechanical property determinations. Destructive tests result in a change in the chemical structure of at least a portion of the tested material. Examples include flammability and chemical resistance tests when the material is not resistant to the tested material.

12.1 SPECTRONIC CHARACTERIZATION OF POLYMERS

12.1.1 INFRARED SPECTROSCOPY

The infrared (IR) spectral range spans the region bound by the red end of the visible region to the microwave region at the lower frequencies (Picture 12.1). Molecular interactions that involve vibrational modes correspond to this energy region. Infrared spectroscopy, IR, is one of the most common spectronic techniques used today to identify polymer structure. Briefly, when the frequency of incident radiation of a specific vibration is equal to the frequency of a specific molecular vibration, the molecule absorbs the radiation. Today, most IR machines are rapid scan where the spectra are Fourier transformed. For the most part, IR band assignments for polymers are analogous to those made for small molecules.

In Fourier transform infrared spectroscopy (FTIR), the light is guided through an interferometer where the signal undergoes a mathematical Fourier transform giving a spectrum essentially identical to the conventional dispersive IR.

With the advent of femtosecond infrared laser pulses, two-dimensional infrared correlative spectroscopy has become a new tool. Here, pump pulses are applied to the sample. After some time that can be from zero to several picoseconds to allow the sample to relax, a second pulse is applied. The result is a 2D plot of the frequency that resulted from the initial pump pulse and a second plot resulting from the relaxed state spectrum. This allows the coupling of various vibrational modes. In some ways, this is similar to two-dimensional NMR spectroscopy in that the spectrum is spread out in two dimensions allowing certain *cross-peaks* to be observed.

Following are brief discussions of some of the more important techniques used in polymer analysis.

Attenuated total reflectance IR (ATR-IR), is used to study films, coatings, threads, powders, interfaces, and solutions (Picture 12.2). (It also serves as the basis of much of the communications systems based on fiber optics.) ATR occurs when radiation enters from a more dense (i.e., a material with a higher refractive index) into a material that is less dense (i.e., with a lower refractive index). The fraction of the incident radiation reflected increases when the angle of incidence increases. The incident radiation is reflected at the interface when the angle of incidence is greater than the critical angle. The radiation penetrates a short depth into the interface before complete reflection occurs. This penetration is called the evanescent wave. Its intensity is reduced by the sample where the sample absorbs.



PICTURE 12.1 FT-IR.



PICTURE 12.2 ATR-FTIR.

ATR imaging is the latest advance in ATR-IR. Instruments are now available that allow spectral images that measure samples to 500 μm diameters. The use of computer enhancement images that show the composition at interfaces of multicomponent samples including paints and laminates is routinely possible while producing traditional ATR-IR spectra.

Specular reflectance IR involves a mirrorlike reflection producing reflection measurements of a reflective material or a reflection–absorption spectrum of a film on a reflective surface. This technique is used to look at thin (from nanometers to micrometers thick) films.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), is used to obtain spectra of powders and rough polymeric surfaces such as textiles and paper. IR radiation is focused onto the surface of the sample in a cup resulting in both specular reflectance (which directly reflects off the surface having equal angles of incidence and reflectance) and diffuse reflectance (which penetrates into the sample subsequently scattering in all angles). Special mirrors allow the specular reflectance to be minimized.

Photoacoustic spectroscopy IR (PAS), is used for highly absorbing materials. Generally, modulated IR radiation is focused onto a sample in a cup inside a chamber containing an IR-transparent gas such as nitrogen or helium. The IR radiation absorbed by the sample is converted into heat inside the sample. The heat travels to the sample surface and then into the surrounding gas causing expansion of the boundary layer of gas next to the sample surface. The modulated IR radiation thus produces intermittent thermal expansion of the boundary layer creating pressure waves that are detected as photoacoustic signals.

PAS spectra are similar to those obtained using ordinary FTIR except truncation of strong absorption bands occurs because photoacoustic signal saturation often occurs. PAS allows the structure to be studied at different thicknesses because the slower the frequency of modulation, the deeper the penetration of IR radiation.

Emission infrared spectroscopy is used for thin films and opaque polymers. The sample is heated so that energy is emitted. The sample acts as the radiation source and the emitted radiation is recorded giving spectra similar to those of classical FTIR. In some cases, IR frequencies vary because of differences in the structures at different depths and interactions between surface and interior emissions.

Infrared microscopy allows the characterization of minute amounts of a material or trace contaminants or additives. Samples as small as 10 μm can be studied. The microscope, often using fiber optics, allows IR radiation to be pinpointed.

Today, there are many so-called hyphenated methods with IR. Hyphenated methods involving IR include GC-IR where the IR spectra are taken of materials as they are evolved through the column. Related to this are HPLC-IR, TG-IR, and MS-IR.

12.1.2 RAMAN SPECTROSCOPY

Raman spectroscopy is similar to IR spectroscopy in that it investigates polymer structure focusing on the vibrational modes (Picture 12.3). Whereas IR is a result of energy being absorbed by a molecule from the ground state to an excited state, Raman spectroscopy is a scattering phenomenon where the energy of photons is much larger than the vibrational transition energies. Most of these photons are scattered without change (so-called Rayleigh scattering). Even so, some are scattered from molecular sites with less energy than they had before the interaction resulting in Raman–Stokes lines. Another small fraction of photons have energies that are now greater than they originally had leading to the formation of anti-Stokes lines. Only the Raman–Stokes photons are important in Raman spectroscopy. While many chemical sites on a polymer are both IR and Raman active, that is, they both give rise to bands, some are less active or even nonactive because of the difference between groups that can absorb and those that scatter. These differences are generally described in terms of symmetry of vibration. Briefly, an IR absorption occurs only if there is a change in the dipole moment during the vibration, whereas a change in polarizability is required for Raman scattering to occur. Even so, the spectra are generally similar and a comparison of the two allows for additional structural characterization beyond that obtained from either of the techniques alone.

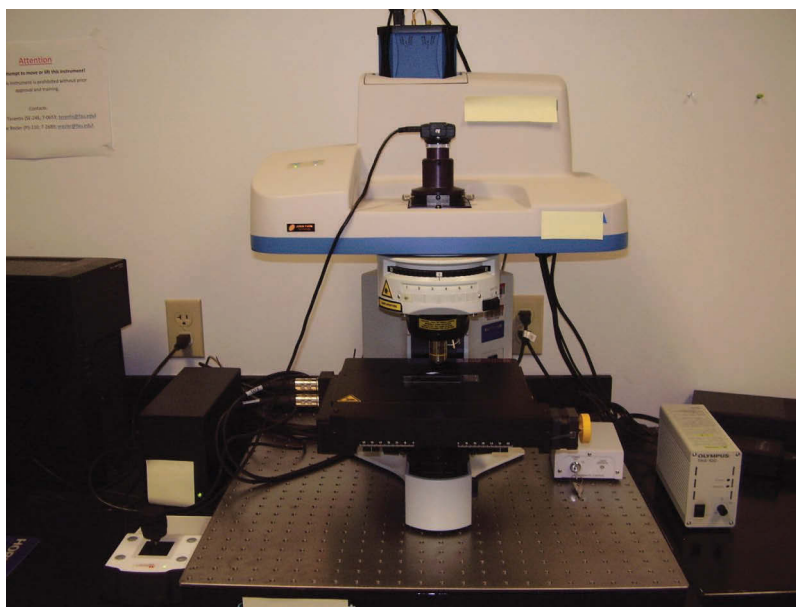
Carraher and Williams showed that for many polymers, differences in symmetry and band production were similar for small molecules as they were for the same groups found in polymers. Thus, observations from the literature and for small model compound studies are generally applicable to similar moieties present in polymeric systems for both Raman and IR spectral analyses.

As in the case with IR spectrometers, there exists a wide variety of specialty techniques especially applicable to polymer analysis.

In **surface-enhanced Raman spectroscopy (SERS)**, samples are adsorbed onto microscopically roughened metal surfaces. Spectra are the intensities and frequencies of scattered radiation originating from a sample that has been irradiated with a monochromatic source such as a laser. SERS spectra are of molecules that are less than 50 Å from the surface.

12.1.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for polymer structure characterization (Picture 12.4). Certain isotopes have two or more energy states available when exposed to a magnetic field. The transitions between these energy states are the basis for NMR.



PICTURE 12.3 Raman spectrometer assembly.



PICTURE 12.4 NMR spectrometer.

These magnetically active nuclei have a property called spin. As a consequence of this spin, these nuclei have an angular momentum and magnetic moment. The ratio of these two properties is called the magnetogyric ratio. Each isotope has a distinct magnetogyric ratio that varies a little with the particular chemical environment in which they are placed.

While NMR has been a strong characterization tool for polymers for many years, it has increased in its usefulness because of continually improved instrumentation and techniques. When a nucleus is subjected to a magnetic field, two phenomena are observed—Zeeman splitting and nuclear precession. Zeeman splitting creates $2I + 1$ magnetic energy states where I is the spin quantum number. When the atomic mass and atomic number are even numbers, $I = 0$ so that these nuclei are unable to have multiple energy levels when exposed to a magnetic field. Thus, ^{12}C , which has both an even atomic number and atomic mass, is NMR inactive, whereas ^{13}C , which has an uneven atomic mass, is NMR active. Nuclear precession is the motion of a spinning body whose axis of rotation changes orientation. The precessional frequency is equal to the magnetic field strength times the magnetogyric ratio.

In a magnetic field, NMR active nuclei can be aligned with the magnetic field (low-energy state) or aligned against the field (high-energy state). At room temperature, there are slightly more nuclei in the lower energy state than in the higher energy state. As magnetic energy is supplied that corresponds to the energy gap (quantum level) between the low- and high-energy states, some nuclei in the low-energy state move to the high-energy state resulting in an absorption of energy, which is recorded as an NMR spectra. The difference between the two energy states is related to the strength of the external magnet. Better spectra are obtained when instruments with larger magnetic fields are employed.

Because of the small but consistent concentrations of carbon 13 present in all organic compounds, it is necessary to use more sophisticated NMR spectroscopy for determining the effect of neighboring electrons on these nuclei. However, ^{13}C -NMR spectroscopy is a valuable tool for investigating polymer structure.

Following is a short description of some of the newer advances.

Nuclear Overhauser effect: The nuclear Overhauser effect (NOE) only occurs between nuclei that share a dipole coupling, that is, their nuclei are so close that their magnetic dipoles interact. Techniques that use NOE enhance ^{13}C spectra and allow spatial relationships of protons to be determined.

Two-dimensional NMR: Basically, the two-dimensional NMR techniques of nuclear Overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) depend on the observation that spins on different protons interact with one another. Protons that are attached

to adjacent atoms can be directly spin coupled and thus can be studied using the COSY method. This technique allows assignment of certain NMR frequencies by tracking from one atom to another. The NOESY approach is based on the observation that two protons closer than about 0.5 nm perturb one another's spins even if they are not closely coupled in the primary structure. This allows spatial geometry to be determined for certain molecules.

The use of actively shielded magnetic field gradients has made the use of pulsed field gradients possible. The use of pulsed field gradients reduces experiment time, minimizes artifacts, and allows for further solvent suppression.

Pulsed NMR: In pulsed NMR the magnetic field is turned on for the time necessary to rotate the magnetization vector into a plane called the 90° rotation or 90° pulse. The field is turned off and the magnetization vector rotates at a nuclear precession frequency relative to the coil. This induces an NMR signal that decays with time as the system returns to equilibrium. This signal is called the “free induction decay” (FID).

After a sample is excited, the spin loses excess energy through interactions with the surroundings eventually returning to its equilibrium state. This process is exponential and is called “spin–lattice relaxation.” The decay is characterized by an exponential time constant.

Two-dimensional experiments allow for more precise determination of coupling relationships. Such experiments are carried out by collecting a series of FID spectra. The time between the pulses is called the “evolution time.” The evolution time is systematically increased as each successive FID is obtained. Each new FID shows a continued change in the couplings in the polymer. The FID spectra are treated using Fourier transformation. A new series of FID spectra are now created by connecting points for each spectra, and these new FIDs are again treated by Fourier transformation producing two-dimensional spectra that are often presented as contour plots. Nuclei that share J-coupling produce a correlation peak. Such approaches allow better interpretation of dipole couplings, molecular diffusion, J-coupling, and chemical exchange.

Solids: Many polymers are either difficultly soluble or insoluble. NMR of solids generally give broad lines because of the effects of dipolar coupling between nuclei and the effect of **chemical shift anisotropy (CSA)**. Both of these effects are greatly reduced for polymers in solution and allow for decent spectra of soluble polymers in solution.

CSA effects are large for solids and are the result of the directional dependence of electronic shielding. CSA effects are overcome through rapidly spinning the sample at an angle to the magnetic field known as the “magic angle.” Solid probes use spinning rotors to hold and spin the sample. The sample is rotated at the magic angle and spun fast enough to remove CSA effects. High-power decouplers or multiple pulse line narrowing allows the decoupling between protons and carbon by using a series of pulses to average the dipolar interactions through spin reorienting. Cross-polarization uses dipolar coupling to increase the sensitivity of less sensitive nuclei. The combination of cross-polarization and magic angle spinning allows good spectra to be obtained for solid polymers.

12.1.4 NMR APPLICATIONS

The various types of spectroscopes complement one another, sometimes giving *new* information and other times giving similar information. The amount of crystallinity and preference for syndiotactic, isotactic, and atactic structure has been determined employing a number of techniques including x-ray. This information can be correlated with information that can be readily obtained from IR and NMR so that product control can be easily monitored. For instance, NMR spectra of poly(methyl methacrylate), PMMA, made by different synthetic routes give different proton shifts that allow the determination of the amounts of isotactic, syndiotactic, and atactic material. Briefly, production of PMMA via so-called high-temperature free radical polymerization gives a largely atactic material. The proton chemical shifts for the α -methyl appear at about 8.8, 8.9, and 9.1 (chemical shifts are based on the tetramethylsilane peak having a value of 10.00 ppm). Largely isotactic PMMA produced using anionic polymerization shows an enhanced peak at about 8.8 that is assigned to the configuration where the α -methyl group in the PMMA repeat unit is flanked on both sides by units of the same configuration. It is the major peak in the 8.8–9.1 triad. PMMA produced employing low-temperature free radical polymerization gives largely syndiotactic product. The peak at 8.9 is assigned to the α -methyl present in a

heterotactic configuration so that the units on either side of it are unlike the central mer since it now becomes the major peak. The 9.1 peak is the largest for the higher temperature product produced via free radical polymerization and is due to the triad central unit being flanked by a like and unlike mer.

Today's NMR capability allows the determination of additional structural features in solution and solid state including the identification of end groups, branches, and defects.

Combinations of solid-state NMR and IR allow the molecular description of the effect of stress–strain and exposure to various conditions including chemical treatments, radiation, and heat on materials.

12.1.5 ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Electron paramagnetic resonance, or electron spin resonance, spectroscopy is a valuable tool for measuring the relative abundance of unpaired electrons present in macromolecules. For example, macroradicals are formed by the homogeneous cleavage of nylon 66 chains when these filaments are broken, with the concentration of macroradicals increasing as the stress is increased.

12.1.6 X-RAY SPECTROSCOPY

X-ray diffraction is a widely used tool for structural identification for almost all solids under the right conditions. X-ray diffractometers are generally either single crystal or powder.

Single-crystal studies allow the absolute configurational determination of polymeric materials that have high degrees of crystallinity. Such determinations are costly with respect to time because of the complexity of polymeric materials.

Powder x-ray spectroscopy can employ smaller crystalline samples from one to several hundred nanometers. These crystallites have broadened peak profiles as a result of incomplete destructive interference at angles near the Bragg angle defined as

$$(12.1) \quad n\lambda = 2d \sin \theta$$

where

n is the order of a reflection

λ the wavelength

d the distance between parallel lattice planes

θ the angle between the incident beam and a lattice plane known as the Bragg angle

This broadening allows determination of crystallite size and size distribution. (Note that this is not particle size.)

X-ray analysis of proteins and nucleic acids is especially important as the absolute structure is needed for many advances in the field of medicine and biochemistry.

12.2 SURFACE CHARACTERIZATION

Everything has a surface or an interface. These surfaces have their own kinetic and thermodynamic features that affect their formation and behavior. Sperling notes that for most polymers, the end groups reside perpendicular to the bulk of the polymers probably because the end is less hydrophobic compared to the bulk and the polymer surfaces generally are *faced* with an air atmosphere that is more hydrophilic. When a polymer solution is deposited onto a surface to *dry*, the concentration has an influence on the orientation of the polymer chains at the surface in the dried solid. Thus, when the amount of polymer is small, the polymer chain lays parallel to the surface in a so-called “pancake” form (Figure 12.1). As the concentration increases, the surface is not able to accommodate the entire polymer chain and it begins to form an inner tangled chain with only the end and some of the chain segments facing the surface forming a *mushroom* shape.

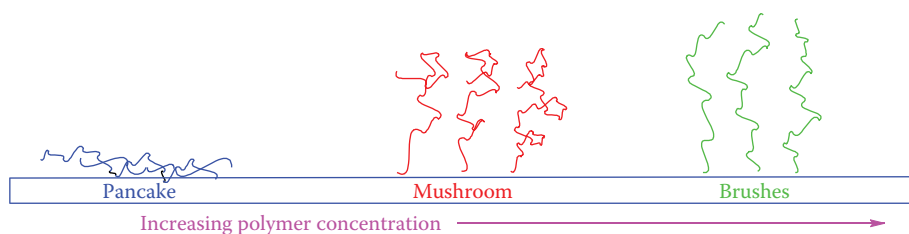


FIGURE 12.1 General surface structures as a function of polymer concentration.

Finally, as the concentration of polymer increases, only the ends of the polymer chains occupy the surface with the polymer ends forming *brushes*.

There is no exact, universally accepted definition of a surface. Here, the surface will be defined as the outermost atomic layers, including absorbed foreign atoms. The chemical and physical composition, orientation, and properties of surfaces typically differ from those of the bulk material.

Current surface characterization techniques fall into two broad categories—those that focus on the outermost few layers (to within the 10–20 layer boundary) and those whose focus includes components present to several thousand angstroms into the solid (hundred to several hundred layers).

12.2.1 ATTENUATED TOTAL REFLECTANCE

Attenuated total reflectance (ATR) typically employs special cells fitted onto traditional IR, FTIR, or UV instruments. While some outer surface aspects are gleaned from such techniques, information to several thousand angstroms is also present in the spectra from ATF.

Techniques that analyze the first few atomic layers generally involve low-energy electrons or ions since the incident radiation should penetrate only the top few layers. Normally a combination of techniques is employed to clearly define the composition of the outer layers. Special precautions are employed to minimize sample surface contamination.

Following is a brief presentation of some of these modern surface characterization techniques.

12.2.2 AUGER ELECTRON SPECTROSCOPY AND X-RAY PHOTOELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are two principal surface analysis techniques. They are used to identify the elemental composition, that is, the amount and nature of species present at the surface to a depth of about 1 nm.

In Auger transitions, incident electrons interact with the inner shell electrons (E_i) of the sample. The vacancy created by an ejected inner shell electron is filled by an outer shell electron (E_1), and a second outer shell electron (E_2) is ejected leaving the atom in a doubly ionized state. The electrons ejected from the outer shells are called Auger electrons, named after the Frenchman Pierre Auger, who discovered the effect. Thus, AES measures the energies of the Auger electrons (E_a) emitted from the first 10 Å of a sample surface. The energy equation is expressed as

$$(12.2) \quad E_a = E_1 - E_i + E_2$$

The kinetic energies of these ejected electrons originating within the first 30 Å of the sample surface are measured by XPS. In XPS, a sample is bombarded by a beam of x-rays with energy $h\nu$ and core electrons are ejected with a kinetic energy E_k that overcomes the binding energy E_b and the work function (ϕ). These core electrons are called x-ray photoelectrons. The energy equation is expressed as follows:

$$(12.3) \quad E_k = h\nu - E_b - \phi$$

The energies of these photoelectrons are reflected relative to the environment of the atoms present at the surface.

12.2.3 NEAR-FIELD SCANNING OPTICAL MICROSCOPY

Optical microscopes have one serious drawback, their resolution, resulting from the fundamental physics of lenses. Lord Rayleigh, over 100 years ago, defined the presently accepted maximum optical lens resolution to be one half the wavelength of the imaging radiation. In truth, conventional optical microscopy did not achieve this level of definition mainly because of out-of-focus light. This prevented the observation of atoms and single molecules.

Near-field scanning optical microscopy (NSOM), allows an extension of optical microscopy to near that of electron microscopy. The central feature is the optical element that is similar, and sometimes the same, to that employed in atomic force microscopy (AFM). Essentially, light is directed through the probe tip onto the sample from just immediately above the sample surface. The light emanating from the probe tip is smaller than the light's wavelength and spreads out over the surface. This results in the maximum influence occurring at the surface with little contribution from regions nearby (such as within 30 nm) resulting in little out-of-focus light. Depending upon the surface and sample thickness, the light is measured as absorption or fluorescence and collected and recorded electronically. NSOM can be fitted onto a regular optical microscope or coupled with scanning probe microscopy (SPM).

12.2.4 ELECTRON MICROSCOPY

The upper limit of magnification for optical microscopes is about 2000 times. Thus, additional forms of microscopy have been developed that allow near to actual atomic observation of polymer surfaces. Electron microscopy utilizes an electron beam to act as the sensing radiation in place of light. High-energy electrons take on wave character as they approach the speed of light. The wavelength is inversely proportional to the electron speed or velocity. When accelerated over large voltages, electrons can be made to travel at speeds to permit wavelengths on the order of 0.003 nm. The electron beam is focused and the image is formed using magnetic lenses. The two most common forms of electron microscopy are transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

In **SEM**, the surface of the polymeric surface is scanned using an electron beam with the reflected or back scattered beam of electrons collected and displayed on a cathode ray tube screen. The image represents the surface contour of the scanned material. Because the surface must be conductive, most polymer surfaces must be overlaid with a conductive coating. Magnifications up to about 50,000 are carried out using SEM.

TEM utilizes an image formed by an electron beam that passes through the sample. This allows internal microstructures to be determined. Structural details of materials can be observed on an atomic level by looking at contrasts in the image caused by various concentrations of different elements. Very thin films are employed. Under good conditions, magnifications up to one million are possible employing TEM.

12.2.5 SCANNING PROBE MICROSCOPY

SPM encompasses a group of surface detection techniques that include **AFM** and **scanning tunneling microscopy (STM)** that allows topographic profiling of surfaces. SPM techniques investigate only the outermost few atomic layers of the surface with nanometer resolutions and, at times, atomic-level resolution.

STM is generally used with electrically conductive materials applied to polymeric materials giving overlays consisting of conducting material layered over the surface of the sample. STM experiments typically require extremely low pressures less than 1×10^{-10} mbar. By comparison, AFM can be run under room conditions and does not require the use of electrically conductive material. As with STM, the metallic tip is held close (about 0.5–1 nm) to the surface. A voltage, applied between the tip and sample surface, drives a tunneling current. The conductive surface reconstructs the atomic positions via minimizing the surface free energy. This gives topographic superstructures with specific electronic states, which are recorded as surface contours or images.

AFM can be run under room conditions. AFM can be performed in either of two forms: a contact mode and a noncontact mode. It does not require the use of electrically conductive material since (in the contact mode) the tip actually *touches* the surface rather than residing immediately above it as is the case in STM. In both the contact and the noncontact modes, light is used as the sensing source rather than an applied voltage. In contact AFM, a cantilever with as sharp a point as possible is laid onto the sample surface with a small loading force in the range of 10^{-7} to 10^{-10} N (newton). Tips of differing size and shape are tailor-made. Data is obtained optically by bouncing an incident laser beam onto the cantilever toward a quadrant detector or in an interferometer. In the noncontact mode, the attractive force is important and the experiment must be carried out under low pressures similar to those employed in STM.

In the contact mode the tip acts as a low-load, high-resolution profiler. Along with structure determination, the AFM is also used to *move* atoms about allowing the construction of images at the atomic level. The AFM is also an important tool in the nanotechnology revolution.

Nanotubes are being used as points in some SPM units. The ends of these nanotubes can be closed or functionalized offering even *finer* tips and tips that interact with specific sites allowing manipulation on an atom-by-atom basis. These nanotubes are typically smaller than silicon tips and are generally more robust.

AFM is useful in identifying the nature and amount of surface objects. AFM, or any of its variations, also allow studies of polymer phase changes, especially thermal phase changes, and results of stress–strain experiments. In fact, any physical or chemical change that brings about a variation in the surface structure can, in theory, be examined and identified using AFM.

Today there exist a wide variety of AFMs that are modifications or extensions of traditional AFM. Following is a brief summary of some of these techniques.

Contact mode AFM is the so-called traditional mode of AFM. Topography contours of solids can be obtained in air and fluids.

Tapping mode AFM measures contours by *tapping* the surface with an oscillating probe tip, thereby minimizing shear forces that may damage soft surfaces. This allows increased surface resolution. This is currently the most widely employed AFM mode.

There are several modes that employ an expected difference in the adhesion and physical property (such as flexibility) as the chemical nature is varied. **Phase imaging** experiments can be carried out and rely on differences in surface adhesion and viscoelasticity. **Lateral force microscopy** measures frictional forces between the probe tip and sample surface. LFM identifies and maps relative differences in surface frictional characteristics. Polymer applications include identifying transitions between different components in polymer blends, composites, and other mixtures, identifying contaminants on surfaces, and looking at surface coatings. **Force modulation** measures differences between the stiffness and elasticity of surface features. **Nanoindenting/scratching** measures mechanical properties by *nanoindenting* to study hardness, scratching, or wear including film adhesion and coating durability.

Noncontact AFM measures the contour through sensing van der Waals attractive forces between the surface and the probe tip held above the sample. It provides less resolution than tapping mode AFM and contact mode AFM.

There are several AFM modes that employ differences in a materials surface electronic and/or magnetic character as the chemical nature of the surface varies. **Magnetic force microscopy** measures the force gradient distribution above the sample. **Electric force microscopy (EFM)** measures the electric field gradient distribution above a sample surface. EFM maps the gradient of the electric field between the tip and the sample surface. The field due to trapped charges, on or beneath the surface, is often sufficient to generate contrast in an EFM image. The voltage can be induced by applying a voltage between the tip and the surface. The voltage can be applied from the microscope electronics under AFM control or from an external power supply. EFM is performed in one of three modes—phase detection, frequency modulation, or amplitude detection. Three-dimensional plots are formed by plotting the cantilever's phase or amplitude as a function of surface location. **Surface potential microscopy, SP**, measures differences in the local surface potential across the sample surface. SP imaging is a nulling technique. As the tip travels above the surface, the tip and the cantilever experience a force whenever the surface potential differs

from that of the tip. The force is nullified by varying the voltage of the tip so that the tip remains at the same potential as the immediate surface. The voltage applied to the tip to maintain this constant potential as the tip surveys the surface with the results plotted as a function of the surface coordinates creating a surface potential image. For best results, SP and EFM do the best job with conductive materials. **Force volume** measurements involve producing two-dimensional arrays of force–distance values allowing a mapping of the force variation and surface topology with individual force curves constructed.

Force–distance microscopy measures repulsive, attractive, and adhesion forces between the time and surface during approach, contact, and separation. This technique combines electrical properties with adhesion/physical properties as a means to study sample surfaces.

Scanning thermal microscopy measures two-dimensional temperature distributions across a sample surface. This is a special thermal technique.

In **electrochemical microscopy**, **ECSTM** and **ECAFM**, the material is immersed in electrolyte solution and the surface and properties of conductive materials are studied.

Information derived from several of these techniques go together to give a clearer idea of the nature of the surface.

AFM results can be utilized in conjunction with other techniques. While some techniques, such as SAXS and small-angle neutron scattering (SANS), allow structural information to be inferred, AFM gives real space results. Some polymeric structural designs may not be unambiguously determined; many can be determined employing ATM. The major limitation concerns whether the structures observed at or near the surface are similar to those in the interior. We are well aware that surface composition differs from the interior composition. For instance, surfaces may be less organized being enriched in chain ends, loops, and switchboard chain segments. Further, for *sliced* samples does the *slicing* disturb the fine structure along the *cut* surface? For instance, the structure of linear polymers such as polyethylene has been suggested to consist of ordered or sharp folds, switchboard-like, loops with loose folds, buttressed loops, and combinations of these features. Magonov and Godovsky and others recently investigated the surface structures of a number of polymers employing ATM. For single crystals of PE, ordered grains 10–12 nm in size are found. For melt-crystallized LLDPE, spherulites of several microns are the major morphological features. Edge-on standing lamellae and lamellar sheets are found. Dark areas are assigned as amorphous regions. The lamellar edges are on the order of 25–40 nm, while the strands are several microns in length. By comparison, melt-crystallized LDPE, which is only about 30% crystalline, shows only spherulitic patterns with ill-defined ring patterns. The grain sizes are about 15–25 nm with fibrillar structures visible. A sample of melt-crystallized ULDPE with low crystallinity (about 15%) gives largely an ill-defined surface consistent of the surface being largely amorphous. As higher force is applied to press through the surface layer, grains of 0–10 nm and finally 9–11 nm become visible with some grains up to about 100–150 nm visible.

Other polymers have been studied. For instance, isotactic polypropylene shows well-defined spherulites with grains (15–20 nm) embedded in an amorphous material. The grains are assembled in circles, and in some cases, along the radial direction, an ordered texture exists. PVDF shows numerous spherulites with fibrils 12–15 nm in width. The granular nanostructure of spherulites has also been found for polyesters and polyurethanes. ATM and other studies (including WAXS and SAXS) suggest that the nanoscale grains are elementary building blocks of the crystalline architecture in most polymers. These grains or blocks can have more or less structure within them. The overall crystalline structure may be developed as a one-dimensional assembling of grains into fibrils and the two-dimensional structures an assembling of grains into lamella.

Spin-cast films of poly(ethylene oxide), PEO, show a flat crystalline morphology with lamellar sheets of different shapes. When melted and then cooled, PEO crystallizes with a similar morphology except the lamellar sheets are smaller. When it is again melted and cooled, crystallization proceeds more slowly and the PEO morphology is dominated by spiral crystallites formed via a screw dislocation mechanism. In all cases, the thickness of the lamellar sheets is about 12 nm indicating multiple folding of the PEO chains. The lamellar sheets disappear at about 60°C though the melting point is listed to be 70°C. On cooling, the lamellar structures reappear about 50°C.

The morphology of spin-cast film, thickness of 180 nm, from polycaprolactone shows many spherulitic structures with fibrillar nanostructures formed of lamellae lying edge on (about 10 nm thick) and areas with lamellar sheets lying flat on. Different crystalline structures are found when the sample is melted and crystallized as a function of temperature. These two studies reinforce the complex inner relationship between physical treatment and nanostructure.

While some structures show seemingly independent spherulitic structures on the surface, we know from other studies that these structures are connected to one another and to the more amorphous regions overall giving a material with a characteristic flexibility and strength. In general, chains are shared with adjacent areas allowing a sharing of stress–strain factors.

AFM is important for biological systems as well as synthetic macromolecules. Several examples are given to illustrate applications. Collagen is an important natural protein that is present in many tissues including bones, skin, tendons, and the cornea. It is also employed in medical devices such as artificial skin, tendons, cardiac valves, ligaments, hemostatic sponges, and blood vessels. There are at least 13 different types of collagen. ATF can image collagen molecules and fibers and their organization allowing identification of the different kinds of collagen and at least surface interactions.

AFM allows the study of cell membranes. The precise organization of such cell membranes is important since they play a role in cell communication, replication, and regulation. It is possible to study real-time interactions of such biologically important surfaces. Further, bilayers, modeled or containing naturally produced bilayers, are used as biosensors. Again, interactions of these biomembranes can be studied employing AFM. For instance, the degradation of bilayers by phospholipases, attachment of DNA, etc., can be studied on a molecular level. In another application, antibody–antigen interactions have been studied employing AFM. One application of this is the creation of biosensors to detect specific interactions between antigens and antibodies.

12.2.6 SECONDARY ION MASS SPECTROSCOPY

Secondary ion mass spectroscopy, SIMS, is a sensitive surface analysis tool. Here, the mass analysis of negative and positive ions sputtered from the polymer surface through ion bombardment is analyzed. The sputtering ion beam is called the primary ion beam. This beam causes erosion of the polymer surface removing atomic and molecular ions. Then these newly created ions, composing what is called the secondary ion beam surface, are analyzed as a function of mass and intensity. Depth of detection for SIMS is of the order of 20–50 Å. Because it is the ions in the secondary ion beam that are detected, the mass spectra obtained from SIMS are different from those obtained using simple electron impact methods. The extent of particular ion fragments observed is dependent on a number of factors including the ionization efficiency of the particular atoms and molecules composing the polymer surface.

SIMS can detect species that are present on surfaces of the order of parts per million to parts per billion.

12.2.7 SUPERRESOLUTION FLUORESCENCE MICROSCOPY

The 2014 Nobel Prize was given to Eric Betzig, Stefan Hell, and William Moerner for developing the technique known as superresolution fluorescence microscopy. While the technique is based on photoswitchable fluorescent proteins, it is chemistry focused on proteins. There are a number of related techniques that are based on photoswitchable fluorescent proteins. Photoactivated localization microscopy activates these proteins a few and at a time for fluorescent proteins that are separated sufficiently that their locations can be precisely determined. The image of the protein is obtained by repeating the cycle many times resulting in an image created by superimposing these images. The initial approaches gave good two-dimensional pictures of the proteins. Later developments allow three-dimensional images to be created.

12.3 AMORPHOUS REGION DETERMINATIONS

Experimental tools that have been employed in an attempt to characterize amorphous regions are given in Table 12.1. Techniques such as birefringence and Raman scattering give information related to the short-range (less than 20 Å) nature of the amorphous domains, while techniques such as neutron scattering, electron diffraction, and electron microscopy give information concerning the longer range nature of these regions.

Birefringence measures order in the axial, backbone direction. The birefringence of a sample can be defined as the difference between the refractive indices for light polarized in two directions 90° apart. Thus, a polymer sample containing polymer chains oriented in a preferential direction by stretching or some other methods will exhibit a different refractive index along the direction of preferred chain alignment compared to that obtained at right angles. This change in birefringence gives information concerning the amount of order, thus information about disorder.

SANS results indicate that vinyl polymers exist in random coils in the amorphous state. Results from electron and x-ray diffraction studies show diffuse halos consistent with the nearest-neighbor spacings being somewhat irregular. It is possible that short-range order and long-range disorder exist within these amorphous regions.

12.4 THERMAL ANALYSIS

Because polymeric materials are expected to perform under a variety of temperature conditions, thermal properties are important. Thermal property investigations can also allow better design of materials that meet the thermal requirements and may also give added structural data.

Major instrumentation involved with the generation of thermal property behavior of materials includes thermogravimetric analysis (TG, TGA) (Picture 12.5), differential scanning calorimetry (DSC), differential thermal analysis (DTA), torsional braid analysis (TBA), thermomechanical analysis (TMA), thermogravimetric–mass spectrometry analysis, and pyrolysis gas chromatography (PGC). Most of these analytic techniques measure the polymer response as a function of time, atmosphere, and temperature.

One of the simplest techniques is PGC in which the gases, resulting from the pyrolysis of a polymer, are analyzed by gas chromatography. This technique may be used for qualitative and quantitative analysis. The latter requires calibration with known amounts of a standard polymer pyrolyzed under the same conditions as the unknown.

There are several different modes of thermal analysis described as DSC. DSC is a technique of nonequilibrium calorimetry in which the heat flow into or away from the polymer is measured as a function of temperature, atmosphere, and/or time. This differs from DTA where the temperature difference between a reference and a sample is measured. Even so, the distinction is not always clear. DSC equipment measures the heat flow by maintaining a thermal balance between the reference and sample by changing a current passing through the heaters under the two chambers. For instance, the heating of a sample and a reference proceeds at a predetermined rate until

TABLE 12.1 Techniques Employed to Study the Amorphous Regions of Polymers

Short-Range Interactions	Long-Range Interactions
Magnetic birefringence	Electron diffraction
Raman scattering	Wide-angle x-ray scattering
Depolarized light scattering	Electron microscopy
Rayleigh scattering	Density
Brillouin scattering	Small-angle neutron scattering
NMR relaxation	
Small-angle x-ray scattering	



PICTURE 12.5 Simultaneous DSC/TGA thermal analyzer.

heat is emitted or consumed by the sample. The circuitry is programmed to give a constant temperature between the reference and sample compartments. If an endothermic occurrence takes place, such as the melting of the sample, the temperature of the sample will be less than that of the reference. Less current is given to the sample, and the amount of the decrease reflects the amount of energy needed to melt the sample. The amount of energy required to melt the sample is generally given as the area under the resulting curve. The advantages of DSC and DTA over a good adiabatic calorimeter include speed, low cost, and the ability to use small samples.

The resultant plot of ΔT as a function of temperature is known as a thermogram. Figure 12.2 contains such a thermogram emphasizing the T_g and T_m endothermic regions for a polymer sample that is approximately 50% crystalline. Several things should be noted. First, the magnitude of the T_m is greater than T_g because it requires more energy to gain entire chain mobility than to achieve segmental mobility. There is a small exothermic region after the T_g that reflects a tendency to form crystalline micelles when there is sufficient mobility to allow their formation.

Possible determinations from DSC/DTA measurements include (1) heat of transition, (2) heat of reaction, (3) sample purity, (4) phase diagram, (5) specific heat, (6) sample identification, (7) percentage incorporation of a substance, (8) reaction rate, (9) rate of crystallization or melting, (10) solvent retention, and (11) activation energy. Thus, thermocalorimetric analysis can be a useful tool in describing the chemical and physical relationship of a polymer with respect to temperature.

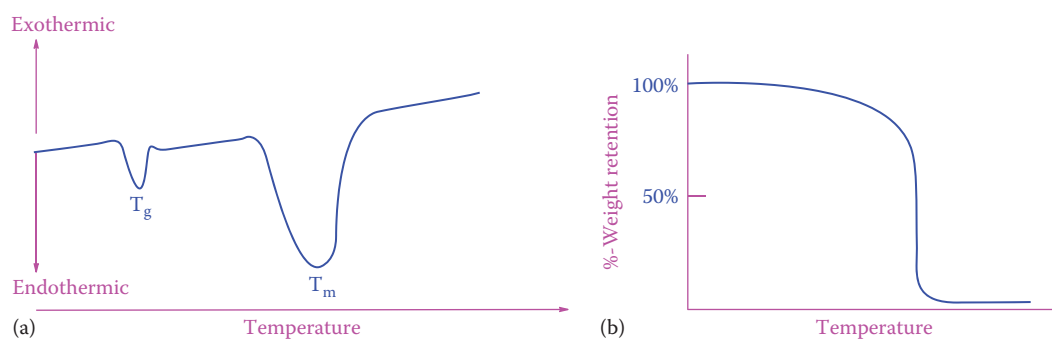


FIGURE 12.2 (a) Illustrative DCS thermogram. (b) TGA thermogram for a typical vinyl polymer.

In TGA, a sensitive balance is used to follow the weight change of a polymer as a function of time, atmosphere, or temperature. Figure 12.2b shows a typical TGA thermogram for a vinyl polymer such as PE. For such polymers where there is a similar thermal energy stability of the backbone, the TGA decrease generally occurs with one downward sweep beginning at about 200°C and being complete before 300°C. There is normally some residue that is high in carbon content remaining to over 1000°C.

Along with a determination of the thermal stability of the polymer, TGA can be used to determine the following: (1) sample purity, (2) identification, (3) solvent retention, (4) reaction rate, (5) activation energy, and (6) heat of reaction.

TMA measures the mechanical response of a polymer looking at (1) expansion properties including the coefficient of linear expansion; (2) tension properties such as measurement of shrinkage and expansion under tensile stress, that is, elastic modulus; (3) volumetric expansion, that is, specific volume; (4) single-fiber properties; and (5) compression properties such as measuring the softening or penetration under load.

In TBA changes in structure are measured. The name TBA is derived from the fact that measurements were initially made of fibers that were *braided* together to give the test samples connected between or onto vicelike attachments or hooks.

Reading and coworkers have pioneered in the adaptation of nano-associated AFM for thermal analyses. The tip of the AFM is replaced with a miniature resistive heater that is used to heat or measure temperature differences on a nanoscale. This allows differentiation between phases and (at times) individual polymer chains and segments (such as block and graft segments of copolymers). T_g and T_m and melting are based on differences in thermal conductivity and diffusivity. This technique of using the microthermal sensor, MTDSC, is called calorimetric analysis with scanning microscopy (CASM). The probe can also be used to measure certain mechanical properties performing a microthermal mechanical analysis with scanning microscopy (MASH).

Newer techniques are being developed and modifications of existing techniques continue.

Softening ranges are dependent on the technique and procedure used to determine them. Thus, listings of softening ranges should be accompanied with how they were determined. Following are some of the techniques used to determine softening ranges. While DSC gives a more precise measurement of not only the T_g , it often approximates the softening range. The capillary method of determining the melting point of small molecules can also be used to gain some idea as to the softening point. Another related technique is to simply use a Fisher–John melting point apparatus and apply some pressure to a sample contained between two glass slides.

The Vicat needle method consists of determining the temperature at which a standard needle penetrates a sample. In the ring-and-ball method, the softening range is determined by noting the temperature at which the sample, held within a ring, can be forced through the ring by application of a standard force.

12.5 THERMAL PROPERTY TESTS

12.5.1 THERMAL CONDUCTIVITY

As energy in the form of heat, magnetic, or electric is applied to one side of a material, the energy is transmitted to other areas of the sample. Heat energy is largely transmitted through the increased amplitude of molecular vibrations. The heat flow Q from any point in a solid is related to the temperature gradient, dt/dl through the thermal conductivity λ as follows:

$$(12.4) \quad Q = -\lambda \frac{dt}{dl}$$

The transmission of heat is favored by the presence of ordered lattices and covalently bonded atoms for organic compounds. Thus, graphite, quartz, and diamond are good thermal conductors, while less ordered forms such as glass have lower thermal conductivities.

12.5.2 THERMAL EXPANSION

Coefficients of thermal expansion generally refer to differences in length, area, or volume as a function of a temperature unit. Relative to metals such as steel, polymers have large coefficients of thermal expansions. Polymers also have quite varied coefficients of thermal expansion. Both of these factors are troublesome when different materials are bound together, including composites, and exposed to wide temperature ranges. Such wide temperature ranges regularly occur in the aerospace industry (aircraft), within computer chips (and many other electrical devices), engines, motors, etc. Thus, it is critical to match the coefficients of thermal expansions of materials that are to be bound through mechanical (such as screws and bolts) and chemical (polymer blends, alloys, adhered through the use of an adhesive) means or stress will develop between the various components resulting in fracture or separation.

For polymeric materials, factors that restrict gross movement, such as cross-linking, typically result in lowered coefficients of expansion. Thus, the typical range for coefficients of expansion for cross-linked thermosets is lower than the typical range found for thermoplastics. Further, materials such as glass, graphite, and concrete also exhibit low coefficients of expansion for the same reason.

12.5.3 GLASS TRANSITION TEMPERATURES

Qualitatively, the T_g corresponds to the onset of short-range (typically one to five chain atoms) coordinated motion. Actually, many more (often 10–100) chain atoms may attain sufficient thermal energy sufficient to move in a coordinated manner at T_g . The T_g (ASTM D-3418) is the temperature at which there is an absorption or release of energy as the temperature is raised or lowered, respectively. The T_g can be measured by any means that allows changes in the conformation of the chains to be detected. Thus, most of the thermal techniques allow T_g to be determined. Also, most spectral techniques also allow T_g to be determined as well as techniques that measure volume changes. Dynamic mechanical spectroscopy is also used to measure chain changes by subjecting the sample to repeated small-amplitude strains in a cyclic fashion as a function of temperature. The polymer molecules store some of the imparted energy and dissipate a portion in the form of heat. Since the amount of energy stored and converted to heat is related to molecular motion, changes in the ratios of energy stored to energy converted to heat are used to measure T_g . Sperling compared literature reports of T_g values for some common polymers and found differences of several decades of degrees in the reported T_g values.

12.6 FLAMMABILITY

Since many polymeric materials are used as clothing, household items, components of automobiles and aircraft, etc., flammability is an important consideration. Some polymers such as polytetrafluoroethylene and PVC are *naturally* flame resistant, but most common polymers such as PE and PP are not. Small-scale horizontal flame tests have been used to estimate the flammability of solid (ASTM D-635), cellular (ASTM D-1692-74), and foamed (ASTM D-1992) polymers, but these tests are useful for comparative purposes only. Large-scale tunnel tests (ASTM E-84) are more accurate, but they are also more expensive to run than ordinary laboratory tests cited before.

One of the most useful laboratory flammability tests is the oxygen index (OI) test (ASTM D-2043 and ASTM D-2863). In this test, the polymer is burned by a candle in controlled mixtures of oxygen and nitrogen. The minimum oxygen concentration that produces downward flame propagation is considered the OI or ignitability of the polymer.

12.7 ELECTRICAL PROPERTIES: THEORY

Polymers have served as important materials in the electronics industry. Generally, they have served as coating and containers because of their lack of conductivity; that is, they are nonconductors. More recently, polymers have become major materials as conductors.

Some important dielectric behavior properties are dielectric loss, loss factor, dielectric constant, direct current (DC) conductivity, alternating current (AC) conductivity, and electric breakdown strength. The term “dielectric behavior” usually refers to the variation of these properties as a function of frequency, composition, voltage, pressure, and temperature.

The dielectric behavior is often studied by employing charging or polarization currents. Since polarization currents depend on the applied voltage and the dimensions of the condenser, it is customary to eliminate this dependence by dividing the charge, Q , by the voltage, V , to get a parameter called the capacitance (capacity, C):

$$(12.5) \quad C = \frac{Q}{V}$$

and then using the dielectric constant ϵ , which is defined as

$$(12.6) \quad \epsilon = \frac{C}{C_0}$$

where

C is the capacity of the condenser when the dielectric material is placed between its plates in a vacuum

C_0 is the empty condenser capacity

Dielectric polarization is the polarized condition in a dielectric resulting from an applied AC or DC field. The polarizability is the electric dipole moment per unit volume induced by an applied field or unit effective intensity. The molar polarizability is a measure of the polarizability per molar volume; thus, it is related to the polarizability of the individual molecules or polymer repeat unit.

Conductivity is a measure of the number of ions per unit volume and their average velocity in the direction of the applied field. Polarizability is a measure of the number of bound charged particles per cubic unit and their average displacement in the direction of the applied field.

There are two types of charging currents and condenser charges, which may be described as rapidly forming or instantaneous polarizations and slowly forming or absorptive polarizations. The total polarizability of the dielectric is the sum of contributions due to several types of charge displacement in the materials caused by the applied field. The relaxation time is the time required for polarization to form or disappear. The magnitude of the polarizability, k , of a dielectric is related to the dielectric constant, ϵ , as follows:

$$(12.7) \quad k = \frac{3(\epsilon - 1)}{4\pi(\epsilon + 2)}$$

The terms “polarizability constant” and “dielectric constant” are often used interchangeably in a qualitative discussion of the magnitude of the dielectric constant. The k values obtained utilizing DC and low-frequency measurements are a summation of electronic (E), atomic (A), dipole (D), and interfacial (I) polarizations as shown in Figure 12.3. Only the contribution by electronic polarizations is evident at high frequencies. The contributions to dielectric constant at low frequencies are additive as shown in Figure 12.3.

Instantaneous polarization occurs when rapid (less than 10^{-10} seconds) transitions occur, that is, at frequencies greater than 10^{10} Hz or at wavelengths less than 1 cm. Electronic polarization falls within this category and is due to the displacement of charges within the atoms. **Electronic polarization** is directly proportional to the number of bound electrons in a unit volume and inversely proportional to the forces binding these electrons to the nuclei of the atoms.

Electronic polarization occurs so rapidly that there is no observable effect of time or frequency on the dielectric constant until frequencies are reached that correspond to the visible and UV spectra. For convenience, the frequency range of the infrared through the UV region is called the optical frequency range, and the radio and the audio range is called the electric frequency range. Electronic polarization is an additive property dependent on the atomic bonds. Thus, the

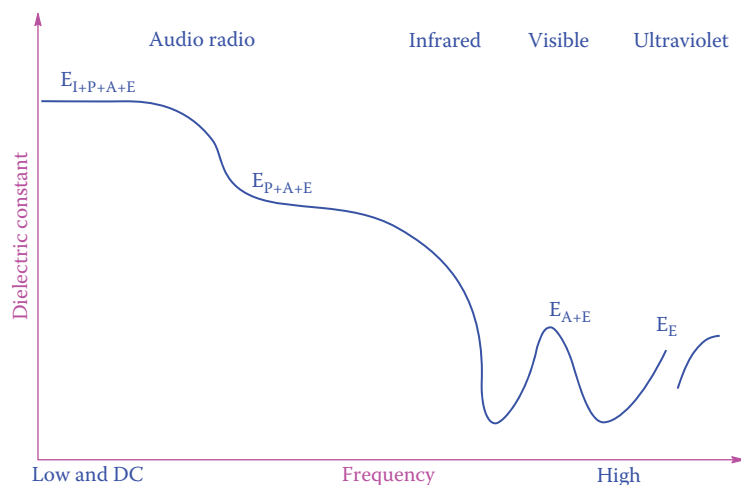


FIGURE 12.3 Relationship of dielectric constant with frequency emphasizing interfacial (I), dipole (P), atomic (A), and electronic (E) polarization contributions.

electronic polarizations and related properties are similar for both small molecules and polymers. Accordingly, values obtained for small molecules can be applied to analogous polymeric materials. This does not apply when the polymeric nature of the material plays an additional role in the conductance of electric charges, as in the case for whole-chain resonance or whole-chain delocalization of electrons.

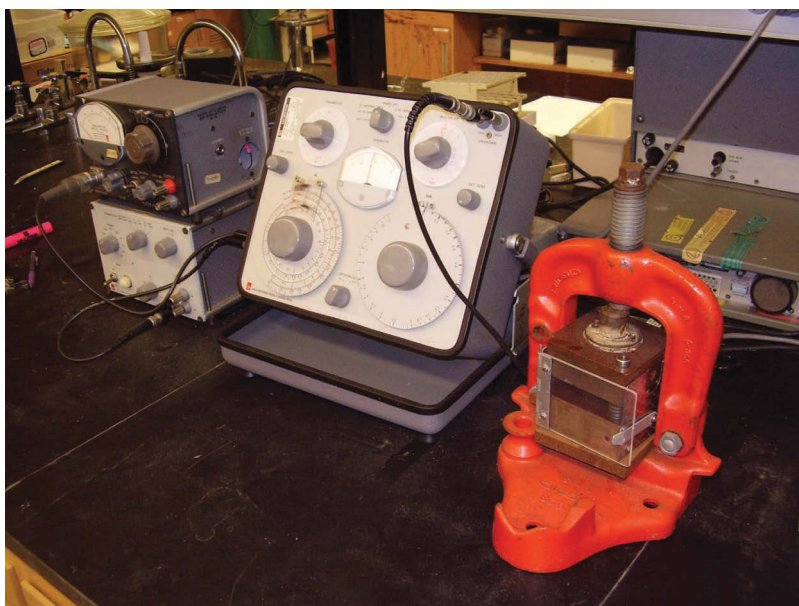
Atomic polarization contributes to the relative motion of atoms in the molecule affected by perturbation by the applied field of the vibrations of atoms and ions having a characteristic resonance frequency in the infrared region. The atomic polarization is large in inorganic materials, which contain low-energy conductive bonds, and approaches zero for nonconductive polymers. The atomic polarization is rapid, and this, as well as the electronic polarization, constitutes the instantaneous polarization components.

The remaining types of polarization are absorptive types with characteristic relaxation times corresponding to relaxation frequencies. Debye, in 1912, suggested that the high dielectric constants of water, ethanol, and other highly polar molecules was due to the presence of permanent dipoles within each individual molecule and that there is a tendency for the molecules to align themselves with their dipole axes in the direction of the applied field. The major contributions to **dipole polarizations** are additive and are similar whether the moiety is within a small or large (macromolecule) molecule. Even so, the secondary contributions to the overall dipole polarization of a sample are dependent on both the chemical and physical environment of the specific dipole unit, its size, and its mobility. Thus, dipole contributions can be used to measure the T_g and T_m .

The polarizations noted earlier are the major types found in homogeneous materials. Other types of polarization, called **interfacial polarizations**, are the result of heterogeneity. Ceramics, polymers with additives, and paper are considered to be electrically heterogeneous.

12.8 ELECTRIC MEASUREMENTS

Material response is typically studied using either direct (constant) applied voltage (DC) or alternating applied voltage (AC) (Picture 12.6). The AC response as a function of frequency is characteristic of a material. In the future, such electric spectra may be used as a product identification tool, much like infrared spectroscopy. Factors such as current strength, duration of measurement, specimen shape, temperature, and applied pressure affect the electric responses of materials. The response may be delayed because of a number of factors including the interaction between polymer chains, the presence within the chain of specific molecular groupings, and the effects related to interactions in the specific atoms themselves. A number of properties, such as relaxation time,



PICTURE 12.6 Electrical property measuring assembly.

power loss, dissipation factor, and power factor, are measures of this lag. The movement of dipoles (related to the dipole polarization, P) within a polymer can be divided into two types: an orientation polarization (P') and a dislocation or induced polarization.

The relaxation time required for the charge movement of electronic polarization E to reach equilibrium is extremely short (about 10^{-15} seconds), and this type of polarization is related to the square of the index of refraction. The relaxation time for atomic polarization A is about 10^{-3} seconds. The relaxation time for induced orientation polarization P' is dependent on molecular structure, and it is temperature dependent.

The electric properties of polymers are also related to their mechanical behavior. The dielectric constant and dielectric loss factor are analogous to the elastic compliance and mechanical loss factor. Electric resistivity is analogous to viscosity. Polar polymers, such as ionomers, possess permanent dipole moments. These polar materials are capable of storing more electric energy than nonpolar materials. Nonpolar polymers are dependent almost entirely on induced dipoles for electric energy storage. Thus, orientation polarization is produced in addition to the induced polarization when the polar polymers are placed in an electric field. The induced dipole moment of a polymer in an electric field is proportional to the field strength, and the proportionality constant is related to the polarizability of the atoms in the polymer. The dielectric properties of polymers are affected adversely by the presence of moisture, and this effect is greater in hydrophilic than in hydrophobic polymers.

12.9 WEATHERABILITY

Polymers are used in almost every conceivable environment. They are tested for their ability to interact with radiation, weather, and microorganisms. Weathering includes the ability to resist attacks by freezing and heating cycles, resistance to frictional damage caused by rain and air, and the influence of low and high temperatures as the polymeric materials are used.

Moisture is an important factor for some polymers, especially those with noncarbon backbones, where hydrolysis, and subsequent degradation, can bring about drastic changes in chain length and, consequently, polymer properties. Such attack can occur on the surface and is indicated, as can many chemical attacks, by a discoloration generally followed by crazing and cracking. Other attacks can occur within the matrix with the polymer absorbing moisture.

Resistance to biological attack is important for many polymer applications including almost all of the biomedical applications, food storage and protection, and coatings where microorganism destruction is important. Most synthetic polymers are *naturally* resistant to destruction by microorganisms. This is particularly true for nonpolar polymers, but less so for condensation polymers such as nylons and polyesters where microorganisms may recognize similarities to bonds they ordinarily hydrolyze. Various preservatives and antimicroorganism additives are added, when appropriate, to protect the material against microbial attack. Tests include destructive degradation and simple growth of the microorganism on the material.

12.10 OPTICAL PROPERTY TESTS

Since polymers are often used as clear plastics or coatings and have many applications where transparency is an important property, knowledge of the optical properties of specific polymers is essential. The radiation scale, of course, includes microwave, infrared, ultraviolet, and visible regions. It is important to recognize the difference between refraction (associated with properties such as refractive index) and reflection (associated with properties such as haze). This difference is illustrated in Figure 12.4.

12.10.1 INDEX OF REFRACTION

Optical properties are related to both the degree of crystallinity and the actual polymer structure. Most polymers do not possess color site units, so are colorless and transparent. But some phenolic resins and polyacetylenes are colored, translucent, or opaque. Polymers that are transparent to visible light may be colored by addition of colorants, and some become opaque as the result of the presence of additives such as fillers, stabilizers, moisture, and gases.

Many of the optical properties of a polymer are related to the refractive index, n , which is a measure of the ability of the polymer to refract or bend light as it passes through the polymer. The refractive index n is equal to the ratio of the sine of the angles of incidence, i , and refraction, r , of light passing through the polymer:

$$(12.8) \quad n = \frac{\sin i}{\sin r}$$

The magnitude of n is related to the density of the substance and varies from 1.000 for vacuum and 1.3333 for water to about 1.5 for many polymers and 2.5 for white pigment titanium(IV) oxide

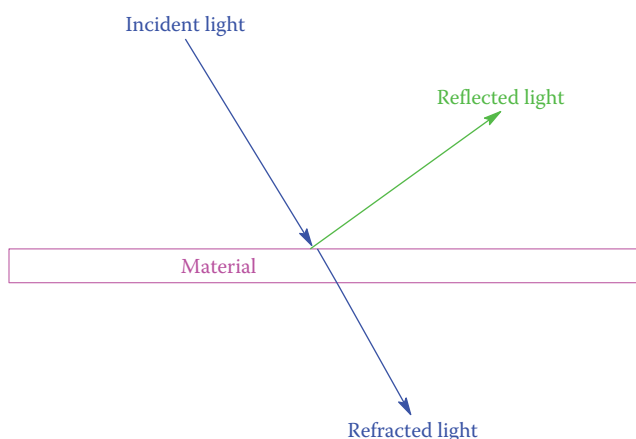


FIGURE 12.4 Refraction and reflection of incident light at the surface of a solid.

(titanium dioxide). The value of n is often high for crystals and is dependent on the wavelength of the incident light and on the temperature. It is usually reported for the wavelength of the transparent sodium D line at 298 K. Typical refractive indices for polymers range from 1.35 for polytetrafluoroethylene to 1.67 for polyarylsulfone.

12.10.2 OPTICAL CLARITY

Optical clarity or the fraction of illumination transmitted through a material is related by the Beer–Lambert relationship:

$$(12.9) \quad \log \frac{I}{I_0} = -AL \text{ and } \frac{I}{I_0} = e^{-AL}$$

where the fraction of illumination transmitted through a polymer (I/I_0) is dependent on the path length of the light (L) and the absorptivity of the polymer at that wavelength of light (A).

Clarity is typical for light passing through a homogeneous material, such as a crystalline ordered polymer or completely amorphous polymer. Interference occurs when the light beam passes through a heterogeneous material in which the polarizability of the individual units varies causing interference that disrupts optical clarity.

12.10.3 ABSORPTION AND REFLECTANCE

Colorless materials range from being almost totally transparent to opaque. The opacity is related to the light scattering process occurring within the material. Incident radiation passes through nonabsorbing, isotropic, optically homogeneous samples with essentially little loss in radiation intensity. Actually, all materials scatter some light. The angular distribution of the scattered light is complex because of the scattering due to micromolecular differences.

Transparency is defined as the state permitting perception of objects through a sample. **Transmission** is the light transmitted. In more specific terms, transparency is the amount of undeviated light, that is, the original intensity minus all light absorbed, scattered, or lost through other means. The ratio of reflected light intensity to the incident light intensity is called the “**absorption coefficient**.”

12.11 CHEMICAL RESISTANCE

The classic test for chemical resistance (ASTM D-543) measures the percentage weight change of test samples after immersion in different liquid systems. Tests for chemical resistance have been extended to include changes in mechanical properties after immersion. Since chemical attack involves changes in chemical structure, it can be readily observed by many instrumental methods that measure chemical structure, in particular surface structure.

Tables 12.2 and 12.3 contain a summary of typical stability values for a number of polymers and elastomers against typical chemical agents. As expected, condensation polymers generally exhibit good stability to nonpolar liquids while they are generally only (relatively) moderately or unstable toward polar agents and acids and bases. This is because of the polarity of the connective *condensation* linkages within the polymer backbone. By comparison, vinyl type of polymers exhibits moderate to good stability toward both polar and nonpolar liquids and acids and bases. This is because the carbon–carbon backbone is not particularly susceptible to attack by polar agents and nonpolar liquids that, at best, will simply solubilize the polymer. All of the materials show good stability to water alone because all of the polymers have sufficient hydrophobic character to repel the water.

TABLE 12.2 Stability of Various Polymers to Various Conditions

Polymer	Nonoxidizing Acid	Oxidizing Acid	Aqueous Salt Sol.	Aqueous Base	Polar Liquids	Nonpolar Liquids	Water
	20% Sulfuric	10% Nitric	NaCl	NaOH	Ethanol	Benzene	
Nylon 66	U	U	S	S	M	S	S
Polytetrafluoroethylene	S	S	S	S	S	S	S
Polycarbonate	M	U	S	M	S	U	S
Polyester	M	M	S	M	M	U	S
Polyetheretherketone	S	S	S	S	S	S	S
LDPE	S	M	S	—	S	M	S
HDPE	S	S	S	—	S	S	S
Poly(phenylene oxide)	S	M	S	S	S	U	S
Polypropylene	S	M	S	S	S	M	S
Polystyrene	S	M	S	S	S	U	S
Polyurethane	M	U	S	M	U	M	S
Epoxy	S	U	S	S	S	S	S
Silicone	M	U	S	S	S	M	S

Note: S, satisfactory; M, moderately to poor; U, unsatisfactory.

TABLE 12.3 Stability of Selected Elastomeric Materials to Various Conditions

Polymers	Weather—	Oxidation	Ozone	NaOH—	Acid—	Degreasers	
	Sunlight					Chlorinated	
	Aging		Cracking	Dil/Con	Dil/Con	Hydrocarbons	Hydrocarbons
Butadiene	P	G	B	F/F	F/F	P	P
Neoprene	G	G	G	G/G	G/G	P	F
Nitrile	P	G	F	G/G	G/G	G	G
Polyisoprene (natural)	P	G	B	G/F	G/F	B	B
Polyisoprene (synthetic)	B	G	B	F/F	F/F	B	B
Styrene- butadiene	P	G	B	F/F	F/F	B	B
Silicone	G	G	G	G/G	G/F	B	F–P

Note: G, good; F, fair; P, poor; B, bad.

SUMMARY

1. The ASTM and comparable organizations throughout the world have established meaningful standards for the testing of polymers.
2. Spectroscopic techniques that are useful for small molecules are equally as important with macromolecules. These techniques give both structural data and data related to the morphology of the polymers.
3. Surface properties are important to the physical and chemical behavior of polymers. Similar to smaller molecules, polymer surface structures can be determined using a variety of techniques including Auger electron spectroscopy, near-field optical microscopy, electron microscopy, SPM, SIMS, and certain IR and MS procedures.
4. Thermal analysis measurements allow the measure of polymer behavior as a function of temperature, time, and atmosphere. DSC/DTA measures changes in energy as temperature is changed and allows the determination of many valuable parameters including T_g and T_m . TGA measures weight changes as a function of temperature.

5. The electrical properties of materials are important for many of the higher technological applications. Measurements can be made using alternating and/or direct current. The electrical properties are dependent on voltage and frequency. Important electrical properties include dielectric loss, loss factor, dielectric constant, conductivity, relaxation time, induced dipole moment, electrical resistance, power loss, dissipation factor, and electrical breakdown. Electrical properties are related to polymer structure. Most organic polymers are nonconductors, but some are conductors.
6. Important physical properties of polymers include weatherability, chemical resistance, and optical properties. Polymers generally show good to moderate chemical resistance when compared to metals and nonpolymers.

GLOSSARY

AES: Auger electron spectroscopy.

AFM: Atomic force microscopy.

ASTM: American Society for Testing and Materials.

Attenuated total reflectance IR (ATR-IR): ATR occurs when radiation enters from a more dense. The fraction of the incident radiation reflected increases when the angle of incidence increases. The incident radiation is reflected at the interface when the angle of incidence is greater than the critical angle. The radiation penetrates a short depth into the interface before complete reflection occurs. This penetration is called the evanescent wave. Its intensity is reduced by the sample where the sample absorbs.

BSI: British Standards Institution.

Chemical shifts: Peaks in NMR spectroscopy.

Correlation NMR Spectroscopy (COSY): Depends on the observation that spins on different protons interact with one another allowing two-dimensional spacing to be determined.

Dielectric constant: Ratio of the capacitance of a polymer to that in a vacuum.

Dielectric strength: Maximum applied voltage that a polymer can withstand without structural change.

Differential scanning calorimetry (DSC): Measurement of the difference in changes in the enthalpy of a heated polymer and a reference standard based on power input.

Differential thermal analysis (DTA, DT): Measurement of the difference in the temperature of a polymer and a reference standard when heated.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS): IR radiation is focused onto the surface of the sample resulting in both specular reflectance (which directly reflects off the surface having equal angles of incidence and reflectance) and diffuse reflectance (which penetrates into the sample subsequently scattering in all angles).

Electron microscopy (EM): Utilizes an electron beam to act as the sensing radiation in place of light.

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy: Measures the relative abundance of unpaired electrons present in samples.

Environmental stress cracking: Cracking of polymers.

Fourier transform infrared spectroscopy (FTIR): IR where the light is guided through an interferometer where the signal undergoes a mathematical Fourier transform.

Glass transition temperature: Temperature where the onset of local or segmental mobility begins.

Heat deflection temperature: Temperature at which a sample loaded beam undergoes a definite deflection.

Index of refraction: Ratio of the velocity of light in a vacuum to that in a transparent material or mixture.

Infrared spectroscopy: Technique used for the characterization of polymers based on their molecular vibration and vibration–rotation spectra.

ISO: International Standards Organization.

Loss factor: Power factor multiplied by the dielectric constant.

Moh's scale: Hardness scale ranging from 1 for talc to 10 for diamond.

Near-field scanning optical microscopy (NSOM): Allows an extension of optical microscopy to near that of electron microscopy. The central feature is the optical element that is similar, and sometimes the same, to that employed in atomic force microscopy (AFM).

Nuclear magnetic resonance spectroscopy (NMR): Based on the absorption of magnetic energy by nuclei that have an uneven number of protons or neutrons; this absorption is dependent on the particular chemical structure and environment of the molecule.

Nuclear Overhauser effect (NOE): NOE occurs between nuclei that share a dipole coupling. Techniques that use NOE enhance ^{13}C spectra and allow spatial relationships of protons to be determined. Two-dimensional NMR. Basically, the two-dimensional NMR techniques of nuclear Overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) depend on the observation that spins on different protons interact with one another.

Oxygen index (OI): Test for the minimum oxygen concentration in a mixture of oxygen and nitrogen that will support a candle-like flame of a burning polymer.

Photoacoustic spectroscopy IR, PAS: Modulated IR radiation is focused onto a sample in a cup inside a chamber containing an IR-transparent gas such as nitrogen or helium. The IR radiation absorbed by the sample is converted into heat inside the sample. The heat travels to the sample surface and then into the surrounding gas causing expansion of the boundary layer of gas next to the sample surface. The modulated IR radiation thus produces intermittent thermal expansion of the boundary layer creating pressure waves that are detected as photoacoustic signals.

Power factor: Electrical energy required to rotate the dipoles in a polymer while in an electrostatic field.

Raman spectroscopy: Based on the interaction of vibrational modes of molecules with relative high-energy radiation where absorption is based on the chemical moieties that undergo changes in polarization.

Scanning electron microscopy (SEM): The surface of a sample is scanned using an electron beam with the reflected or back scattered beam of electrons collected and displayed on a cathode ray tube screen.

Scanning probe microscopy (SPM): Group of surface detection techniques that includes AFM and STM; measures surface depth differences.

Secondary ion mass spectroscopy (SIMS): Mass spectroscopy that looks at the ion fragments generated from the bombardment of surfaces with an ion beam.

Thermogravimetric analysis (TG, TGA): Measurement of the change in weight when a polymer is heated.

XPS: X-ray photoelectron spectroscopy; also known as ESCA.

EXERCISES

1. Why are electrical tests for polymers important?
2. Which is the better insulator: a polymer with (a) a low or (b) high K factor?
3. Why are the specific heats of polymers higher than those of metals?
4. Which IR technique might give you good surface information?
5. Why is the use of the term flameproof plastics incorrect?
6. Which plastic should be more resistant when immersed in 25% sulfuric acid at room temperature: (a) HDPE, (b) PMMA, or (c) PVAc?
7. Why is it important to know the nature and structure of the surface of materials?
8. Why is it important to know such things as the values of thermal expansion of materials?
9. How is NMR important in characterizing polymers?
10. What is the UV region of the spectrum?
11. Which would absorb in the UV region: (a) polystyrene, (b) *Hevea* rubber, or (c) PVC?
12. What technique(s) would you use to determine crystallinity in a polymer?
13. What thermal instrumental technique would you use to determine T_g ?

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Rheology and Physical Tests

13

Throughout this chapter, please remember that the main reasons for studying rheology (stress–strain relationships) are (1) to determine the suitability of materials to serve specific applications and (2) to relate the results to polymer structure and form. Understanding structure–property relationships allows a better understanding of the observed results on a molecular level resulting in a more knowledgeable approach to the design of materials. Another extremely important idea is that the difference in properties between small molecules and polymers is the size that often involves a so-called time constant. Thus, small molecules can move about relatively easily in a melt or solvent but polymers have a long “train” or “body” that must be involved in the movement. Size also allows polymeric memory to occur and assists in describing the overall property of the macromolecules beyond that of simple size. This largeness allows polymers to entangle with one another creating such features as a critical chain length so that polymer chains act in unison and not alone. These, and many more properties, are possible because of the largeness of the polymers. This theme is played out throughout this polymer text and current chapter. Look for these ideas as you study this chapter and text.

Polymers are viscoelastic materials meaning they can act as liquids, the “visco” portion, and as solids, the “elastic” portion. Descriptions of the viscoelastic properties of materials generally fall within the area called rheology. Determination of the viscoelastic behavior of materials generally occurs through stress–strain and related measurements. Whether a material behaves as a “viscous” and/or “elastic” material depends on temperature, the particular polymer and its prior treatment, polymer structure, and the particular measurement or conditions applied to the material. The particular property demonstrated by a material under given conditions allows polymers to act as solid or viscous liquids, plastics, elastomers, fibers, etc. This chapter deals with the viscoelastic properties of polymers.

13.1 RHEOLOGY

The branch of science related to the study of deformation and flow of materials was given the name “**rheology**” by Bingham, whom some have called the father of modern rheology. The prefix *rheo* is derived from the Greek term *rheos*, meaning current or flow. The study of rheology includes two vastly different branches of mechanics called fluid and solid mechanics. The polymer scientist is usually concerned with viscoelastic materials that act as both solids and liquids.

The elastic component is dominant in solids; hence, their mechanical properties may be described by *Hooke’s law* (Equation 13.1), which states that the applied stress (s) is proportional to the resultant strain (γ) but is independent of the rate of this strain ($d\gamma/dt$):

$$(13.1) \quad s = E\gamma$$

Stress is equal to the force per unit area, and *strain* or elongation is the extension per unit length. For an isotropic solid, that is, one having the same properties regardless of direction, the strain is defined by Poisson’s ratio, $V = \gamma_w/\gamma_l$, which is the change in thickness (γ_w ; lateral contraction) compared to the change in length (γ_l).

When there is no volume change, as when an elastomer is stretched, Poisson’s ratio is 0.5. This value decreases as the T_g of the polymer increases and approaches 0.3 for rigid solids such as PVC

and ebonite. For simplicity, the polymers dealt with here will be considered to be isotropic viscoelastic solids with a Poisson's ratio of 0.5, and only deformations in tension and shear will be considered. Thus, a shear modulus (G) will usually be used in place of Young's modulus of elasticity (E ; Equation 13.2) where E is about 2.6 G at temperatures below T_g . For comparison, the moduli (G) for steel, HDPE, and *Hevea* rubber (NR) are 86, 0.087, and 0.0006 dyne/m², respectively:

$$(13.2) \quad ds = G d\gamma \quad \text{and} \quad s = G\gamma$$

The viscous component is dominant in liquids; hence, their flow properties may be described by *Newton's law* (Equation 13.3) where η is the viscosity, which states that the applied stress s is proportional to the rate of strain $d\gamma/dt$, but is independent of the strain γ or applied velocity gradient:

$$(13.3) \quad s = \eta \left(\frac{d\gamma}{dt} \right)$$

Both Hooke's and Newton's laws are valid for small changes in strain or rate of strain, and both are useful in studying the effect of stress on viscoelastic materials. The initial elongation of a stressed polymer below T_g is reversible elongation due to a stretching of covalent bonds and distortion of the bond angles. Some of the very early stages of elongation by disentanglement of chains may also be reversible. However, the rate of flow, which is related to slower disentanglement and slippage of polymer chains past one another, is irreversible and increases (and η decreases) as the temperature increases in accordance with the following form of the Arrhenius equation (13.4), in which E is the activation energy for viscous flow:

$$(13.4) \quad \eta = Ae^{E/RT}$$

It is convenient to use a simple weightless *Hookean*, or ideal, *elastic spring* with a modulus G and a simple *Newtonian* (fluid) *dashpot* or shock absorber having a liquid with a viscosity of η as models to demonstrate the deformation of an elastic solid and an ideal liquid, respectively. The stress–strain curves for these models are shown in Figure 13.1.

In general terms, the Hookean spring represents bond flexing, while the Newtonian dashpot represents chain and local segmental movement. It is customary to attempt to relate stress–strain behavior to combinations of dashpots and springs as indicators of the relative importance of bond flexing and segmental movement.

Again, in general terms, below their T_g polymers can be modeled as having a behavior where the spring portion is more important. Above their T_g where segmental mobility occurs, the dashpot portion is more important.

The relative importance of these two modeling parts, the spring and the dashpot, is also dependent on the rate at which an experiment is carried out. Rapid interaction, such as

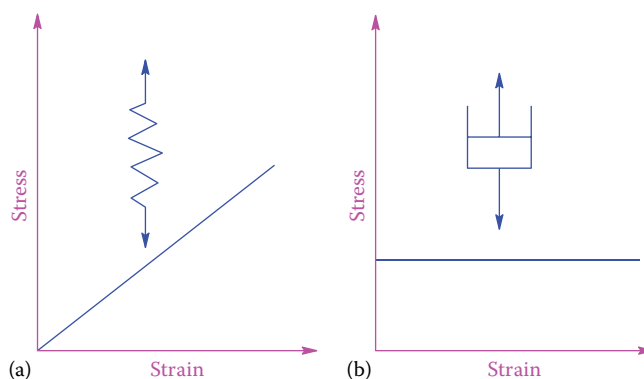


FIGURE 13.1 Stress–strain plots for a Hookean spring (a) where E (Equation 13.1) is the slope and a Newtonian dashpot (b) where s is a constant (Equation 13.3).

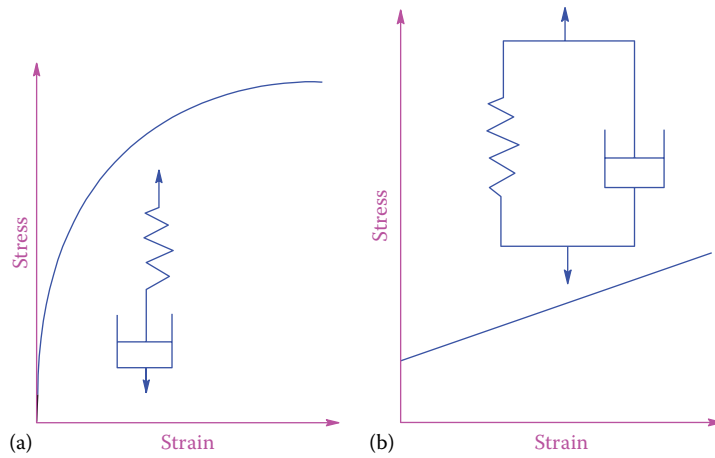


FIGURE 13.2 Stress–strain plot for stress relaxation for the Maxwell model (a) and Voigt–Kelvin model (b).

striking with a hammer, with a polymer is more apt to result in a behavior where bond flexibility is more important, while slow interactions are more apt to allow for segmental mobility to occur.

Since polymers are viscoelastic solids, combinations of these models are used to demonstrate the deformation resulting from the application of stress to an isotropic solid polymer. Maxwell joined the two models in series to explain the mechanical properties of pitch and tar (Figure 13.2a). He assumed that the contributions of both the spring and dashpot to strain were additive and that the application of stress would cause an instantaneous elongation of the spring, followed by a slow response of the piston in the dashpot. Thus, the relaxation time (τ), when the stress and elongation have reached equilibrium, is equal to η/G .

In the *Maxwell model* for viscoelastic deformation, it is assumed that the total strain is equal to the elastic strain plus the viscous strain. This is expressed in the following differential equation (Equation 13.5):

$$(13.5) \quad \frac{d\gamma}{dt} = \frac{s}{\eta} + \frac{ds}{dt} \left(\frac{1}{G} \right)$$

The rate of strain $d\gamma/dt$ is equal to zero under conditions of constant stress (s), that is,

$$(13.6) \quad \frac{s}{\eta} + \frac{ds}{dt} \left(\frac{1}{G} \right) = 0$$

Then, assuming that $s = s_0$ at zero time, we get

$$(13.7) \quad s = s_0 e^{-tG/\eta}$$

And since the relaxation time $\tau = \eta/G$, then

$$(13.8) \quad s = s_0 e^{-t/\tau}$$

Thus, according to Equation 13.8 for the Maxwell model or element, under conditions of constant strain, the stress will decrease exponentially with time and at the relaxation time $t = \tau$, s will equal $1/e$, or 0.37 of its original value, s_0 .

The parallel dashpot–spring model was developed by Voigt and Kelvin and is known as the “*Voigt–Kelvin model*” (Figure 13.2b). In this model or element, the applied stress is shared between the spring and dashpot, and thus, the elastic response is retarded by the viscous resistance of the liquid in the dashpot. In this model, the vertical movement of the spring is essentially

equal to that of the piston in the dashpot. Thus, if G is much larger than η , the retardation time (η/G) or τ is small, and τ is large if η is much larger than G .

In the Voigt–Kelvin model for viscoelastic deformation, it is assumed that the total stress is equal to the sum of the viscous and elastic stress, $s = s_v + s_0$, so that

$$(13.9) \quad s = \eta \left(\frac{d\gamma}{dt} \right) + G\gamma$$

On integration, one obtains

$$(13.10) \quad \gamma = \frac{s}{G(1 - e^{-tG/\eta})} = \frac{s}{G(1 - e^{-t/T})}$$

The *retardation time* τ is the time for the strain to decrease to $1 - (1/e)$ or $1 - (1/2.7) = 0.63$ of the original value.

The viscoelastic flow of polymers is explained by approximate combinations of the dashpot and spring. The plots of the real data are compared with those predicted by various models. The relative importance of the various components of the model that fits the experimental data indicates the importance of the types of chain movement represented by the dashpot and spring have for that particular polymer under the specified experimental conditions.

13.1.1 RHEOLOGY AND PHYSICAL TESTS

While polymer melts and non-cross-linked elastomers flow readily when stress is applied, structural plastics must resist irreversible deformation and behave as elastic solids when relatively small stresses are applied. These plastics are called “*ideal*” or “*Bingham plastics*” with their behavior described mathematically by

$$(13.11) \quad s - s_0 = \eta \left(\frac{d\gamma}{dt} \right)$$

Figure 13.3 contains the stress–strain plots for a number of important flow behaviors. A Bingham plastic exhibits Newtonian flow above the stress yield or stress value (s_0). Liquids that undergo a decrease in viscosity with time are called “*thixotropic*” or false bodied. Those that undergo an increase in viscosity with time are called “*rheoplectic*” (shear thickening). The term “*creep*” is used

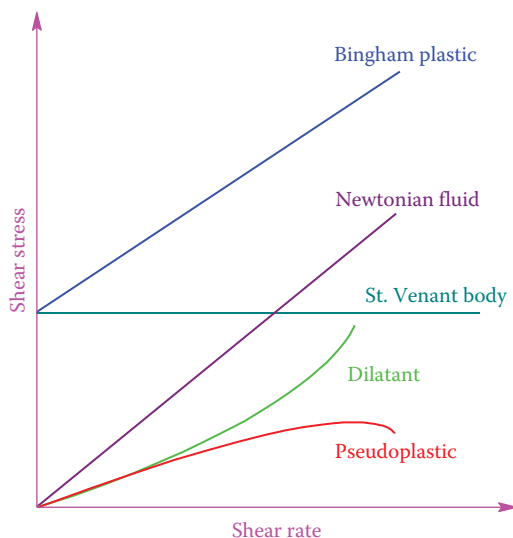


FIGURE 13.3 Various types of polymer flow.

to describe the slow slippage of polymer chains over a long period of time. The Herschel–Buckley equation (Equation 13.12) is a general equation that reduces to the Bingham equation when $\eta = 1$, and to the Newtonian equation when $\eta = 1$ and $s_0 = 0$ and where ϕ is related to viscosity:

$$(13.12) \quad (s - s_0)\eta = \phi \left(\frac{dy}{dt} \right)$$

Eyring explained liquid flow using a random hole-filling model in which the holes (vacancies or free volume) account for about 15% of the total volume at room temperature. The size of these holes is similar to that for small molecules. The number of holes increases as the temperature increases, and thus, flow or hole filling is temperature dependent. Small molecules jump into the holes leaving empty holes when their energy exceeds the activation energy. The activation energy for jumping or moving into a hole is smaller, per individual unit, for linear molecules that fill the holes by successive correlated jumps of chain segments along the polymer chain. The *jump frequency* (ϕ) is governed by a segmental factor with both values related to molecular structure and temperature.

For convenience and simplicity, polymers have generally been considered to be isotropic in which the principal force is shear stress. While such assumptions are acceptable for polymers at low shear rates, they fail to account for stresses perpendicular to the plane of the shear stress, which are encountered at high shear rates. For example, an extrudate such as the formation of a pipe or filament expands when it emerges from the die in what is called the Barus or Weissenberg effect or die swell. This behavior is not explained by simple flow theories.

Viscoelastic behavior can be divided into five subclassifications (Figure 13.4). From 1 to 2, Figure 13.4, the material behaves as a viscous glass or Hookean elastic or glass, where chain segmental motion is quite restricted and involves mainly only bond bending and bond angle deformation. The material behaves as a glass such as window glass.

At 2 (Figure 13.4), the material is undergoing a glassy transition into the rubbery region, 3–4, which is often referred to as the viscoelastic region where polymer deformation is reversible but time dependent and associated with both side chain and main chain rotation. In the rubbery region, local segmental mobility occurs but total chain flow is restricted by a physical and/or chemical network. At 5, rubbery flow or viscous flow occurs where irreversible bulk deformation and slippage of chains past one another occurs. Each of these viscoelastic regions is time dependent. Thus, given a short interaction time, window glass acts as a Hookean glass, that is

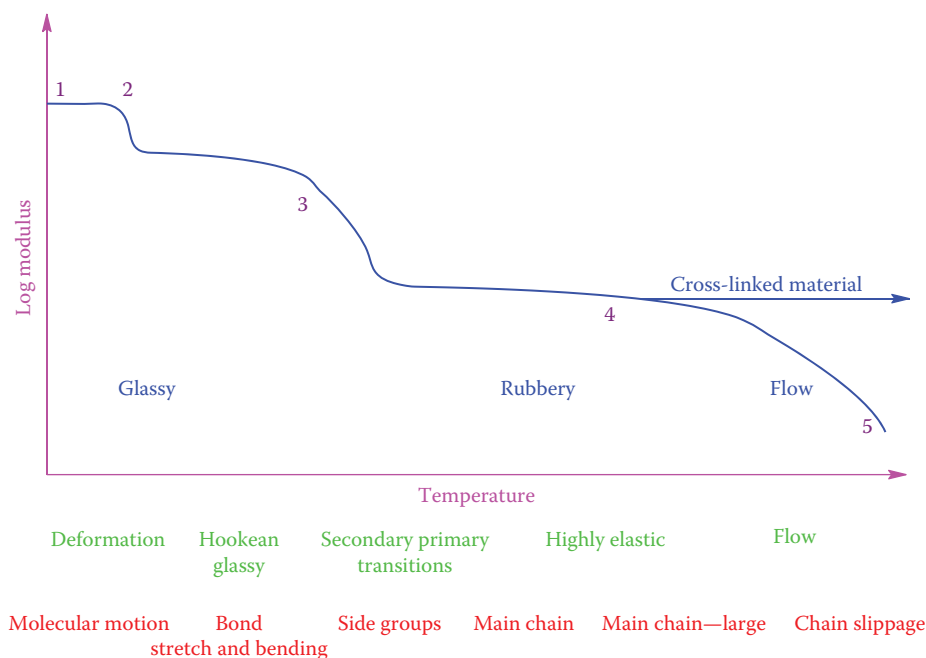


FIGURE 13.4 Characteristic conformational changes as temperature is changed.

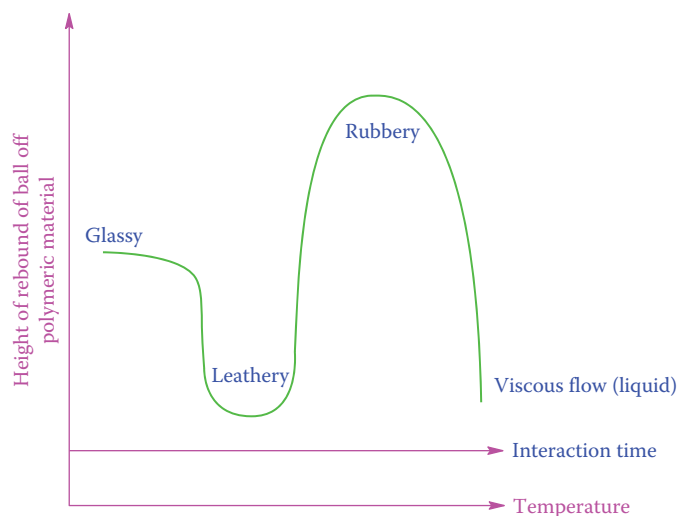


FIGURE 13.5 Regions of material response as a function of interaction (reaction) time and temperature for a typical polymeric material.

like a solid, yet observation of glass over many years would permit the visual observation of flow, with the window glass giving a viscous flow response, thus acting as a fluid. In fact, most polymers give a response as noted in Figure 13.5 when a ball dropped on to the polymeric material at different rates onto the polymeric material as it is heated to different temperatures. Commercial Silly Putty or Nutty Putty easily illustrates three of these regions (Picture 13.1). When struck rapidly, it shatters as a solid (glass region); when dropped at a moderate rate, it acts as a rubber (rubbery region); and when allowed to reside in its container for some time, it flows to occupy the container contour, acting as a liquid. The exact response (Figure 13.5) varies between materials. The leathery region deserves special comment. This region corresponds to the T_g of a material where the impact energy is absorbed resulting in some segmental mobility rather than simply being released resulting in a rebound. The extent of energy absorption is dependent on a number of factors including the proportion of amorphous area.

There have been many attempts to predict long-range behavior from short-range behavior. This is a dangerous practice if the end prediction is material failure because, for most polymeric



PICTURE 13.1 Variable rheology material.

materials, failure is catastrophic and not “well behaved.” But for other properties, application of the Boltzmann time-temperature superposition master curves can be used to some advantage, particularly pertaining to predicting behavior as depicted in Figure 13.5. This transposition for amorphous polymers is accomplished using a shift factor (a_T) calculated relative to a reference temperature T_r , which may be equal to T_g . The relationship of the shift factor to the reference temperature and some other temperature T , which is between T_g and $T_g + 50$ K, may be approximated by the Arrhenius-like equation (13.13):

$$(13.13) \quad \log a_T = - \left(\frac{b}{2.3 T T_g} \right) (T - T_g)$$

According to the more widely used *Williams, Landel, and Ferry equations*, all linear, amorphous polymers have similar viscoelastic properties at T_g . At specific temperatures above T_g , such as $T_g + 25$ K, where the constants C_1 and C_2 are related to holes or free volume, the following relationship holds:

$$(13.14) \quad \log a_T = - \frac{C_1(T - T_g)}{[C_2 + (T - T_g)]}$$

13.1.2 RESPONSE TIME

We can get a first approximation of the physical nature of a material from its response time. For a Maxwell element, the relaxation time is the time required for the stress in a stress-strain experiment to decay to $1/e$ or 0.37 of its initial value. A material with a low relaxation time flows easily so it shows relatively rapid stress decay. Thus, whether a viscoelastic material behaves as a solid or fluid is indicated by its response time and the experimental time scale or observation time. This observation was first made by Marcus Reiner who defined the ratio of the material response time to the experimental time scale as the *Deborah number*, D_n . Presumably, the name was derived by Reiner from the Biblical quote in Judges 5, Song of Deborah where it says, “The mountains flowed before the Lord.”

$$(13.15) \quad D_n = \frac{\text{Response time}}{\text{Experimental time scale}}$$

A high Deborah number designates the solid behavior of a viscoelastic material, while a low Deborah number corresponds to a viscoelastic material behaving as a fluid. Thus, window glass has a high relaxation time at room temperature. Application of a stress to produce a little strain and looking for it to return to its approximate prestressed state will take a long time as we count our observation time in hours, days, and weeks. Thus, it would have a relatively high Deborah number under this observation time scale and acting as a solid. Yet, if we were to have as our observation scale millions of years, the return to the prestressed state would be rapid with the glass acting as a viscous liquid and having a low Deborah number. Again, this represents only a first approximation measure of the behavior of a material.

13.2 TYPICAL STRESS-STRAIN BEHAVIOR

Most physical tests involve nondestructive evaluations. For our purposes, three types of mechanical stress measures (described in Figure 13.6) will be considered. The ratio of stress to strain is called “Young’s modulus.” This ratio is also called the modulus of elasticity and tensile modulus. It is calculated by dividing the stress by the strain:

$$(13.16) \quad \text{Young's modulus} = \frac{\text{Stress (Pa)}}{\text{Strain (mm/mm)}}$$

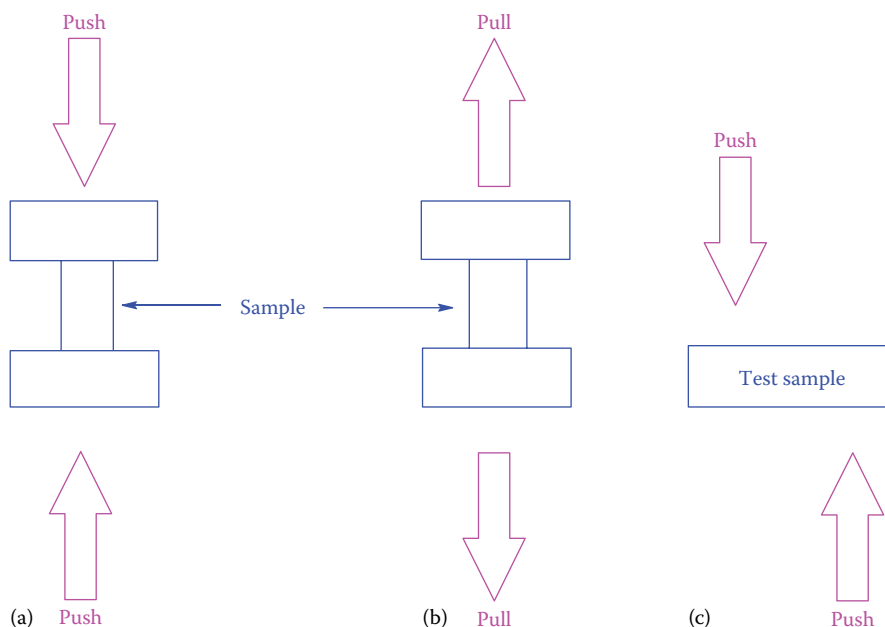


FIGURE 13.6 Major types of stress tests: compressive (a), pulling stress or tensile strength (b), and shear stress (c).

Large values of Young's modulus indicate that the material is rigid and resistant to elongation and stretching. Many synthetic organic polymers have Young's modulus values in the general range of about 10^4 – 10^{10} Pa. For comparison, fused quartz has a Young's modulus of about 10^6 ; cast iron, tungsten, and copper have values of about 10^7 ; and diamond has a value of about 10^8 . Carswell and Nason assigned five classifications to polymers (Figure 13.7). It must be remembered that the ultimate strength of each of these is the total area under the curve before breaking. The soft and weak class, such as polyisobutylene, is characterized by a low modulus of elasticity, low yield (stress) point, and moderate time-dependent elongation. The Poisson's ratio, that is, ratio of contraction to elongation, for soft and weak polymers is about 0.5, which is similar to that found for many liquids.

In contrast, the Poisson's ratio for the hard and brittle class of polymers, such as polystyrene, approaches 0.3. These polymers are characterized by a high modulus of elasticity, a poorly defined yield point, and a little elongation before failure. However, soft and tough polymers, such as plasticized PVC, have a low modulus of elasticity, a high elongation, a Poisson's ratio of about 0.5–0.6,

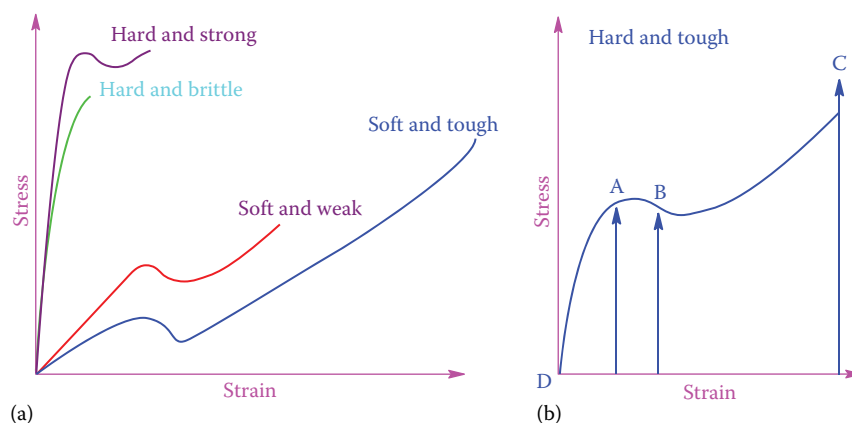


FIGURE 13.7 (a) Typical stress–strain curves for plastics where (b) A is the elongation at yield point, B is the yield stress, C is the elongation at break, and the area under the curve is the ultimate strength.

and a well-defined yield point. Soft and tough polymers stretch after the yield point with the area under the entire curve, toughness or ultimate strength, greater than for the hard and brittle polymers.

Rigid PVC is representative of hard and strong polymers. These polymers have a high modulus of elasticity and high yield strength. The curve for hard and tough polymers, such as ABS copolymers, shows moderate elongation prior to the yield point followed by nonrecoverable elongation.

In general, the behavior of all classes of polymer behavior is Hookean prior to the yield point. The reversible recoverable elongation prior to the yield point, called the elastic range, is primarily the result of bending and stretching of covalent bonds in the polymer backbone. This useful portion of the stress–strain curve may also include some recoverable uncoiling of polymer chains. Irreversible slippage of polymer chains is the predominant mechanism after the yield point.

Since these properties are time dependent, the soft and weak polymers may resemble the hard and strong polymers if the stress is rapidly applied and vice versa. These properties are also temperature dependent. Hence, the properties of soft and tough polymers may resemble hard and brittle when temperature is decreased. The effects of temperature and the mechanisms of elongation are summarized in Figure 13.4.

As noted in Figure 13.6, the major modes for applying stress are axial (compression or tension), flexural (bending or shear), and torsional (twisting; not shown). Superimposed on these can be any number of cyclic arrangements. Several common fluctuating stress–time modes are typically employed. In the regular and sinusoidal time-dependent mode, the stress is applied, as both compressional and torsional, in a regular manner with respect to both time and amount. In a second cyclic arrangement, stress, again both compressional and torsional, is applied in an uneven manner with respect to amount and time so that the maxima and minima are asymmetrical relative to the zero stress level.

Associated with such cyclic application of stress is the term “*fatigue*” to describe the failure that occurs after repeated applications of stress. The fatigue values are almost always less than measurements, such as tensile strength, obtained under static load. Thus, it is important that both static and cyclic measurements be made.

Data are often plotted as stress versus the logarithm of the number of cycles, N , to failure for each sample. Generally, tests are taken using about two-thirds of the static parameter value. There is some limiting stress level below which fatigue does not occur (over some reasonably extended time). This value is called the “*fatigue*” or “*endurance limit*.” The *fatigue strength* is defined as the stress at which failure will occur for some specified number of cycles. *Fatigue life* is the number of cycles that are needed to cause failure.

Polymeric materials are dissimilar to metals in a number of respects. For instance, the range of stress–strain behavior is more complex and varied for polymers. Highly elastic polymers can exhibit a modulus as low as 7 MPa or as high as 100 GPa for stiff polymeric fibers. The modulus values for metals are often higher (50–400 GPa) but not as varied. Tensile strengths for polymers are on the order of 100 MPa for polymers and for some metal alloys, 4000 MPa. By comparison, polymers are more deformable with elastic polymers having elongations in excess of 500%, while even “moldable” metals have elongations not exceeding 100%. Further, stress–strain behavior for polymers is more temperature dependent in comparison to metals. For instance, Figure 13.8 contains the stress–strain behavior for a poly(methyl methacrylate) (PMMA) material. Below the T_g , the material behaves as a stiff, brittle solid similar to the behavior given for hard and brittle polymers (Figure 13.8). As the temperature increases, the PMMA gains enough thermal energy to allow for some segmental mobility. The T_g varies greatly for PMMA depending upon the tacticity with isotactic PMMA having a T_g of about 45°C, and for syndiotactic, the T_g is about 130°C. The material in Figure 13.8 is largely isotactic with a T_g of about 50°C–60°C. By 50°C, the material behaves as a soft and tough material in Figure 13.8.

13.3 STRESS–STRAIN RELATIONSHIPS

Mechanical testing involves a complex of measurements including creep and shear strength and impact strengths. Stress–strain testing is typically carried out using holders where one member is movable. Studies typically vary with either the stress or strain fixed and the result response

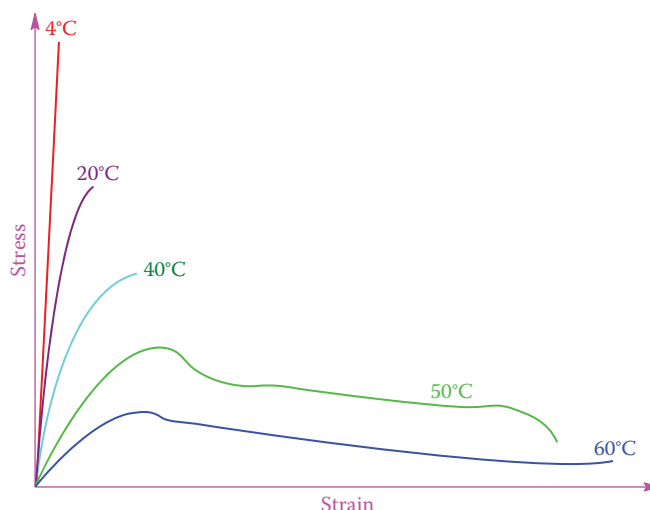


FIGURE 13.8 Influence of temperature on the stress–strain behavior of a sample of poly(methyl methacrylate). (Modeled after Carswell, T.S., Nason, H.K., Effects of environmental conditions on the mechanical properties of organic plastics, in *Symposium on Plastics*, American Society for Testing Materials, Philadelphia, PA, 1944.)

measured. In a variable stress experiment, a sample of given geometry is connected to the grips. Stress, load, is applied, generally by movement of the grip heads either toward one another (compression) or away from one another (elongation). This causes deformation, strain, of the sample. The deformation is recorded as the force/area necessary to achieve this deformation. The applied load versus deformation is recorded and translated into stress–strain curves such as those given in Figures 13.3, 13.7, and 13.8.

For many materials, between their T_g and T_m , recovery is not complete. This incomplete recovery is called “creep.” Creep is time dependent and is described as follows:

$$(13.17) \quad \text{Compliance} = \frac{\text{Stress}}{\text{Strain}}$$

where the compliance and strain are time dependent.

Creep behavior is similar to viscous flow. The behavior shown by Equation 13.1 shows that compliance and strain are linearly related to strain and inversely related to stress. This linear behavior is typical for most amorphous polymers for small strains over short periods of time. Further, the overall effect of a number of such imposed stresses are additive. Non-creep-related recovery occurs when the applied stress is relieved. Thus, amorphous polymers and polymers containing substantial amounts of amorphous regions act as both elastic solids and liquids above their T_g .

Phase changes, phase transitions, refer to changes of state. Most low-molecular-weight materials exist as solids, liquids, and gases. The transitions that separate these states are melting (or freezing) and boiling (or condensing). By contrast, polymers do not vaporize “intact” to a gas, nor do they boil. The state of a polymer, that is, its physical response character, depends on the time allotted for interaction and the temperature as well as the molecular organization (crystalline, amorphous mix). The term “relaxation” refers to the time required for the response to a change in pressure, temperature, or other applied parameter. The term “dispersion” refers to the absorption or emission of energy at a transition. In practice, the terms relaxation and dispersion are often used interchangeably.

An experiment that can be used in the classroom involves the comparison between the bounce of a superball and a ball bearing (Picture 13.2). Drop both from the same height and notice which rebounds the greatest. The ball bearing is typically some metal such as steel and the impact of the drop causes some of the iron atoms to come closer to one another. The rebound is the result of enthalpy forces as the iron atoms pushed back to their original shape. By comparison, the



PICTURE 13.2 Superballs.

superball is tightly packed, random cross-linked polymer chains (high disorder or entropy; the chains are largely polyethylene-like polymer chains) where the impact results in a decreased volume from the repacking of the largely disorganized chains. This is caused by the impact of the dropped ball onto a solid surface forming a more organized (lower entropy), more closely packed, and decreased volume for the polymer chains. The rebound is the result of the now less randomly packed chains returning to the greater disorganized, greater volume, and higher entropy situation causing the rebound. In this situation, the superball is more effective at capturing the energy from the bounce resulting in a higher rebound. This is an example where the cause of a similar physical phenomenon, here the bounce, can be divided largely into the two different primary thermodynamic factors entropy and enthalpy.

13.4 SPECIFIC PHYSICAL TESTS

13.4.1 TENSILE STRENGTH

Tensile strength can be determined by applying force to the material until it breaks as shown in the following equation:

$$(13.18) \quad \text{Tensile strength (Pa)} = \frac{\text{Force required to break sample (N)}}{\text{Cross-sectional area (m}^2\text{)}}$$

Tensile strength, which is a measure of the ability of a polymer to withstand pulling stresses, is usually measured using a dumbbell-shaped specimen (ASTM D-638-72; Figure 13.9). These test specimens are conditioned under standard conditions of humidity and temperature before testing.



FIGURE 13.9 Typical “dumbbell”- or “dog-bone”-shaped sample used for stress–strain measurements.

The *elastic modulus* (also called tensile modulus or modulus of elasticity) is the ratio of the applied stress to the strain it produces within the region where the relationship between stress and strain is linear. The *ultimate tensile strength* is equal to the force required to cause failure divided by the minimum cross-sectional area of the test sample.

13.4.2 TENSILE STRENGTH OF INORGANIC AND METALLIC FIBERS AND WHISKERS

The tensile strength of materials is dependent on the treatment and form of the material. Thus, the tensile strength of isotropic bulk nylon 66 is less than that of anisotropic-oriented nylon 66 fiber. Inorganics and metals also form fibers and whiskers with varying tensile strengths (Table 13.1). Fibers are generally less crystalline and larger than whiskers.

Many of these inorganic fibers and whiskers are polymeric including many of the oxides (including the so-called ceramic fibers), carbon and graphite materials, and silicon carbide. Carbon and graphite materials are similar but differ in the starting materials and the percentage of carbon. Carbon fibers derived from polyacrylonitrile are about 95% carbon, while graphite fibers are formed at higher temperatures giving a material with 99% carbon.

These specialty fibers and whiskers exhibit some of the highest tensile strengths recorded (Tables 13.1 and 13.2); they are employed in applications where light weight and high strength

TABLE 13.1 Tensile Strengths of Inorganic and Metallic Materials as a Function of Form

Material	Form	Tensile Strength (MPa)
Graphite	Bulk	1,000
	Fiber	2,800
	Whisker	15,000
Glass	Bulk	1,000
	Fiber	4,000
Steel	Bulk	2,000
	Fiber	400
	Whisker	10,000

TABLE 13.2 Ultimate Tensile Strength of Representative Organic, Inorganic, and Metallic Fibers

Material	Tensile Strength (MPa)	Tensile Strength/Density
Aluminum silica	4100	1060
Aramid	280	200
Beryllium carbide	1000	400
Beryllium oxide	500	170
Boron-tungsten boride	3450	1500
Carbon	2800	1800
Graphite	2800	1800
UHMW polyethylene	380	3800
Poly(ethylene terephthalate)	690	500
Quartz	900	400
Steel	4000	500
Titanium	1900	400
Tungsten	4300	220

are required. Organics offer weight advantages, typically being less dense than most inorganic and metallic fibers. Uses include dental fillings, the aircraft industry, production of lightweight fishing poles, automotive antennas, lightweight strong bicycles, turbine blades, heat-resistant reentry vessels, and golf club shafts. Many are also used as reinforcing agents in composites.

13.4.3 HARDNESS

The term “hardness” is a relative term. Hardness is the resistance to local deformation that is often measured as the ease or difficulty for a material to be scratched, indented, marred, cut, drilled, or abraded. It involves a number of interrelated properties such as yield strength and elastic modulus. Because polymers present such a range of behavior, they are viscoelastic materials; the test conditions must be carefully described. For instance, elastomeric materials can be easily deformed, but this deformation may be elastic with the indentation disappearing once the force is removed. While many polymeric materials deform in a truly elastic manner returning to the initial state once the load is removed, the range of total elasticity is often small resulting in limited plastic or permanent deformation. Thus, care must be taken in measuring and in drawing conclusions from the results of hardness measurements.

13.4.4 FAILURE

The failure of materials can be associated with a number of parameters. Two major causes of failure are creep and fracture. The tensile strength is the nominal stress at the failure of a material. Toughness is related to ductility. For a material to be tough, it often takes a material having a good balance of stiffness and give.

Calculations have been made to determine the theoretical upper limits with respect to the strength of polymers. Real materials show behaviors near to those predicted by the theoretical calculations during the initial stress–strain determination but vary greatly near the failure of the material. It is believed that the major reasons for the actual tensile strength at failure being smaller than calculated are related to imperfections, the nonhomogeneity of the polymeric structure. These flaws, molecular irregularities, act as the weak link in the polymer’s behavior. These irregularities can be dislocations, voids, physical crack, and energy concentrations. Even with these imperfections, they have high strength-to-mass ratios (Table 13.2), with the highest tensile strength/density value for UHMW polyethylene.

The fracture strengths of polymers are generally lower than those of metals and ceramics. The mode of failure for thermosets is generally referred to as the materials being brittle. Cracks, related to bond breakage, occur at points of excess stress. These create weak spots and may lead to fracture if the applied stress, appropriate to create bond breakage, continues.

Fracture of thermoplastics can occur by either a ductile or brittle fashion or some combination. Rapid application of stress (short reaction time), lower temperatures, and application of the stress by a pointed or sharpened object all increase the chances that failure will occur by a brittle mechanism as expected. For instance, below the T_g , thermoplastics behave as solids, and above T_g , polymer fracture increasingly moves to a ductile mode. Above the T_g , they display some plastic deformation before fracture. For some thermoplastics, crazing occurs prior to fracture. These crazes are a form of defect and are associated with some yielding or void formation either through migration or elimination of some part of the polymer mix or because of chain migration through chain realignment or other mechanism. Fibrillar connections, from aligned chains, often form between void sides. If sufficient stress is continued, these fibrillar bridges are broken and the microvoids enlarge eventually leading to crack formation. Crazes can begin from scratches, flaws, molecular inhomogeneities, and molecular-level voids formed from chain migration (such as through crystallization) or small molecule migration from a site as well as application of stress.

SUMMARY

1. Rheology is the study of deformation and flow of materials. Polymers are viscoelastic materials, meaning they can act as liquids and as solids.
2. Many of the rheological properties of materials are determined using stress–strain measurements.
3. Models are used to describe the behavior of materials. The fluid or liquid part of the behavior is described in terms of a Newtonian dashpot or shock absorber, while the elastic or solid part of the behavior is described in terms of a Hookean or ideal elastic spring.
4. The Hookean spring represents bond flexing, while the Newtonian dashpot represents chain and local segmental movement. In elastomers, the spring also represents chain elongation.
5. In general, the springlike behavior is more important for polymers below their T_g , whereas the dashpot behavior is more important for polymers above their T_g .
6. Mathematical relationships have been developed to relate models composed to varying degrees of these two aspects of behavior to real materials.
7. Stress–strain behavior is closely dependent upon the particular conditions under which the experiment is carried out.
8. There are a number of specific tests that are used to measure various physical properties of materials. Many of these tests are described in detail by the various governing bodies that specify testing procedures and conditions.

GLOSSARY

Barcol impressor: Instrument used to measure the resistance of a polymer to penetration or indentation.

Biaxially stretching: Stretching in two directions perpendicular to each other.

Bingham, E. C.: Father of rheology.

Bingham plastic: Plastic that does not flow until the external stress exceeds a critical threshold value.

Coefficient of expansion: Change in dimensions per degree of temperature.

Compression strength: Resistance to crushing forces.

Creep: Permanent flow of polymer chains.

Dashpot: Model for Newtonian fluids consisting of a piston and a cylinder containing a viscous liquid.

Dilatant: Shear-thickening agent; describes a system where the shear rate does not increase as rapidly as the applied stress.

Elastic range: Area under a stress–strain curve to the yield point.

Flexural strength: Resistance to bending.

Hooke's law: Stress is proportional to strain.

Impact strength: Measure of toughness.

Isotropic: Having similar properties in all directions.

Maxwell element or model: Model in which an ideal spring and dashpot are connected in series; used to study the stress relaxation of polymers.

Modulus: Stress per unit strain; measure of the stiffness of a polymer.

Newtonian fluid: Fluid whose viscosity is proportional to the applied viscosity gradient.

Newton's law: Stress is proportional to flow.

Poisson's ratio: Ratio of the percentage change in length of a sample under tension to its percentage change in width.

Pseudoplastic: Shear-thinning agent: system where the shear rate increases faster than the applied stress.

Relaxation time: Time for stress of a polymer under constant strain to decrease to $1/e$ or 0.37 of its original value.

Retardation time: Time for the stress in a deformed polymer to decrease to 63% of the original value.

Rheology: Science of flow.

Rheopectic: Liquid whose viscosity increases with time.

Shear: Stress caused by planes sliding by each other.

Shear strength: Resistance to shearing forces.

Stress (s): Force per unit area.

Stress relaxation: Relaxation of a stressed sample with time after the load is removed.

Tensile strength: Resistance to pulling stresses.

Thixotropic: Liquid whose viscosity decreases with time.

Velocity gradient: Flow rate.

Viscoelastic: Having the properties of a liquid and a solid.

Voigt–Kelvin model or element: Model consisting of an ideal spring and dashpot in parallel in which the elastic response is retarded by viscous resistance of the fluid in the dashpot.

Williams, Landel, and Ferry equation (WLF): Used for predicting viscoelastic properties at temperatures above T_g when these properties are known for one specific temperature.

Yield point: Point on a stress–strain curve below which there is reversible recovery.

EXERCISES

1. What is the difference between morphology and rheology?
2. Which of the following is viscoelastic: (a) steel, (b) polystyrene, (c) diamond, or (d) neoprene?
3. Define G in Hooke's law.
4. Which would be isotropic: (a) a nylon filament, (b) an extruded pipe, or (c) ebonite?
5. What are the major types of stress tests?
6. Describe in molecular terms what a dashpot represents.
7. Which will have the higher relaxation time: (a) unvulcanized rubber or (b) ebonite?
8. Describe in molecular terms what a spring represents.
9. Define what compliance is.
10. What does viscoelastic mean?
11. Below the glass transition temperature, a material should behave in what manner?
12. At what temperature would the properties of polystyrene resemble those of *Hevea* rubber at 35 K above its T_g ?
13. Define Young's modulus. Should it be high or low for a fiber?
14. Define the proportionality constant in Newton's law.
15. What term is used to describe the decrease of stress at constant length with time?
16. In which element or model for a viscoelastic body, (a) Maxwell or (b) Voigt–Kelvin, will the elastic response be retarded by viscous resistance?
17. What is the most important standards organization in the United States?
18. For most polymeric materials, is failure abrupt or continuous?
19. Is it safe to predict long-range properties from short time period results for plastics?
20. Describe the importance of relating models to stress–strain results.
21. If a sample of polypropylene measuring 5 cm elongates to 12 cm, what is the percentage of elongation?
22. If the tensile strength is 705 kg/cm² and the elongation is 0.026 cm, what is the tensile modulus?
23. Define creep.
24. Briefly describe a Voigt–Kelvin model.
25. What changes occur in a polymer under stress before the yield point?
26. What changes occur in a stress polymer after the yield point?
27. How can you estimate relative toughness of polymer samples from stress–strain curves?
28. What effect will a decrease in testing temperature have on tensile strength?
29. What effect will an increase in the time of testing have on tensile strength?
30. Describe a Maxwell model.

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Additives

Most polymeric materials are not wholly a single polymer, but they contain chemicals added to them to modify some physical, biological, and/or chemical behavior. These added chemicals, or additives, are generally added to modify properties, assist in processing, and introduce new properties to a material. Coloring agents, colorants, are added giving a product or component with a particular color often for identification or ecstastic purposes. Antibacterial agents are added to protect the material from certain microbial attack. Composites contain a fiber and continuous polymer phase resulting in a material that has a greater flexibility and strength than either of the two components. Some of these additives are polymeric while others are not. They may be added as gases, liquids, or solids. Often, some combination of additives is present. A typical tire tread recipe has a processing aid, accelerator, activator, antioxidant, antiozonate, softener, finishing aid, retarder, vulcanizing agent, and accelerator as additives. A typical water-based paint has titanium dioxide as the white pigment; china clay as an extender, a fungicide, a defoaming agent, a coalescing liquid, and a surfactant-dispersing agent; and calcium carbonate as another extender. In total, additives are essential materials that allow the polymeric portion(s) to perform as needed. Some of these additives are present in minute amounts and others are major amounts of the overall composition. Some additives are expensive and others are added to simply give bulk and thus are inexpensive. While the identity, amount, and action of many additives were developed on less than a scientific basis, today adequate scientific knowledge is known so that there is a rational for the use of essentially all additives.

Typical additives include the following:

Antiblocking agents	Lubricants
Antifoaming agents	Mold release agents
Antifogging agents	Odorants or fragrances
Antimicrobial agents	Plasticizers
Antioxidants	Preservatives
Antistatic agents	Reinforcements
Blowing agents	Slip agents
Coloring agents	Stabilizers, including
Coupling agents	Radiation (UV, VIS)
Curing agents	Heat
Fillers	Viscosity modifiers
Flame retardants	Flow enhancers
Foaming agent	Thickening agents
Impact modifiers	Antisag agents
Low-profile materials	

In this chapter, we will look at a variety of additives.

14.1 FILLERS

According to the American Society for Testing and Materials standard ASTM D-883, a filler is a relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities or to lower costs, while a reinforced plastic is one with some strength

properties greatly superior to those of the base resin resulting from the presence of high-strength fillers embedded in the composition. The word extender is sometimes used for fillers. Also, the notion that fillers simply “fill” without adding some needed property is not always appropriate. Some fillers are more expensive than the polymer resin and do contribute positively to the overall properties.

Both natural and synthetic fillers are used. Examples of such fillers are given in Table 14.1.

Among the naturally occurring filler materials are cellulosics, such as wood flour, α -cellulose, shell flour, starch, and proteinaceous fillers such as soybean residues. Approximately 40,000 tons

TABLE 14.1 Types of Fillers for Polymers

I. Organic materials	B. Silicates
A. Cellulosic products	1. Minerals
1. Wood products	a. Asbestos
a. Kraft paper	b. Kaolinite (china clay)
b. Chips	c. Mica
c. Course flour	d. Talc
d. Ground flour	e. Wollastonite
2. Comminuted cellulose products	2. Synthetic products
a. Chopped paper	a. Calcium silicate
b. Diced resin board	b. Aluminum silicate
c. Crepe paper	C. Glass
d. Pulp preforms	1. Glass flakes
3. Fibers	2. Solid and hollow glass spheres
a. α -Cellulose	3. Milled glass fibers
b. Pulp performs	4. Fibrous glass
c. Cotton flock	a. Filament
d. Textile by-products	b. Rovings and woven rovings
e. Jute	c. Yarn
f. Sisal	d. Mat
g. Rayon	e. Fabric
B. Lignin-type products-processed lignin	D. Metals
C. Synthetic fibers	E. Boron fibers
1. Polyamides (nylons)	F. Metallic oxides
2. Polyesters	1. Ground material
3. Polyacrylonitrile	a. Zinc oxide
D. Carbon	b. Alumina
1. Carbon black	c. Magnesia
a. Channel black	d. Titania
b. Furnace black	2. Whiskers (including nonoxide)
2. Ground petroleum coke	a. Aluminum oxide
3. Graphite filaments	b. Beryllium oxide
4. Graphite whiskers	c. Zirconium oxide
II. Inorganic materials	d. Aluminum nitride
A. Silica products	e. Boron carbide
1. Minerals	f. Silicon carbide and nitride
a. Sand	g. Tungsten carbide
b. Quartz	h. Beryllium carbide
c. Tripoli	G. Calcium carbonate
2. Synthetic materials	1. Chalk
a. Wet-processed silica	2. Limestone
b. Pyrogenic silica	3. Precipitated calcium carbonate
c. Silica aerogel	H. Polyfluorocarbons
	I. Barium ferrite and sulfate

of cellulosic fillers are used annually by the US polymer industry. Wood flour, which is produced by the attrition grinding of wood wastes, is used as filler for phenolic resins, urea resins, polyolefins, and PVC. Shell flour, which lacks the fibrous structure of wood flour, has been used as a replacement for wood flour for some applications.

α -Cellulose, which is more fibrous than wood flour, is used as filler for urea and melamine plastics. Melamine dishware is a laminated structure consisting of molded resin-impregnated paper. Presumably, the formaldehyde in these thermosetting resins reacts with the hydroxyl groups in cellulose producing a more compatible composite. Starch and soybean fillers have been used to make biodegradable composites and other materials.

Carbon black, which was produced by the smoke impingement process by the Chinese over 1000 years ago, is now the most widely used filler for polymers. Much of the 1.5 million tons produced annually is used for the reinforcement of elastomers. The most widely used carbon black is furnace carbon black.

Conductive composites are obtained when powdered metal fillers, metal flakes, or metal-plated fillers are added to resins. These composites have been used to produce forming tools for the aircraft industry and to overcome electromagnetic interference in office machines.

Calcium carbonate is available as ground natural limestone and as a synthetic chalk. It is widely used in paints, plastics, and elastomers. The volume relationship of calcium carbonate to resin or the pigment volume required to fill voids in the resin composite is called the pigment-volume concentration.

14.2 REINFORCEMENTS

According to the ASTM definition, fillers are relatively inert while reinforcements improve the properties of the materials to which they are added. Actually, few fillers are used that do not improve properties, but reinforcing fibers produce dramatic improvements to the physical properties of the material to which it is added, generally to form composites.

The transverse modulus (M_T) and many other properties of a long fiber–resin composite may be estimated from the law of mixtures. The longitudinal modulus (M_L) may be estimated from the Kelly Tyson equation (Equation 14.1) where the longitudinal modulus is proportional to the sum of the fiber modulus (M_F) and the resin matrix modulus (M_M). Each modulus is based on a fractional volume (c). The constant k is equal to 1 for parallel continuous filaments and decreases for more randomly arranged shorter filaments:

$$(14.1) \quad M_L = kM_Fc_F + M_Mc_M$$

Since the contribution of the resin matrix is small in a strong composite, the second term in the Kelly Tyson term can be disregarded. Thus, the longitudinal modulus is dependent on the reinforcement modulus, which is independent of the diameter of the reinforcing fiber.

As noted before, for the most part, the resulting materials for the use of reinforcements are composites. Composites are materials that contain strong fibers embedded in a continuous phase. The fibers are called “reinforcement” and the continuous phase is called the matrix. While the continuous phase can be a metallic alloy or inorganic material, the continuous phase is typically an organic polymer that is termed a “resin.” Because of the use of new fibers and technology, most of the composites discussed here are referred to as “space-age” and “advanced materials” composites. Composites can be fabricated into almost any shape and after hardening, they can be machined, painted, etc., as desired.

While there is a lot of science and “space-age technology” involved in the construction of composites, many composites have been initially formulated through a combination of this science and “trial-and-error” giving “recipes” that contain the nature and form of the fiber and matrix materials, amounts, additives, and processing conditions.

Composites have high tensile strengths (on the order of thousands of MPa), high Young’s modulus (on the order of hundreds of GPa), and good resistance to weathering exceeding the bulk properties of most metals. The resinous matrix, by itself, is typically not particularly strong relative to the composite. Further, the overall strength of a single fiber is low. In combination,

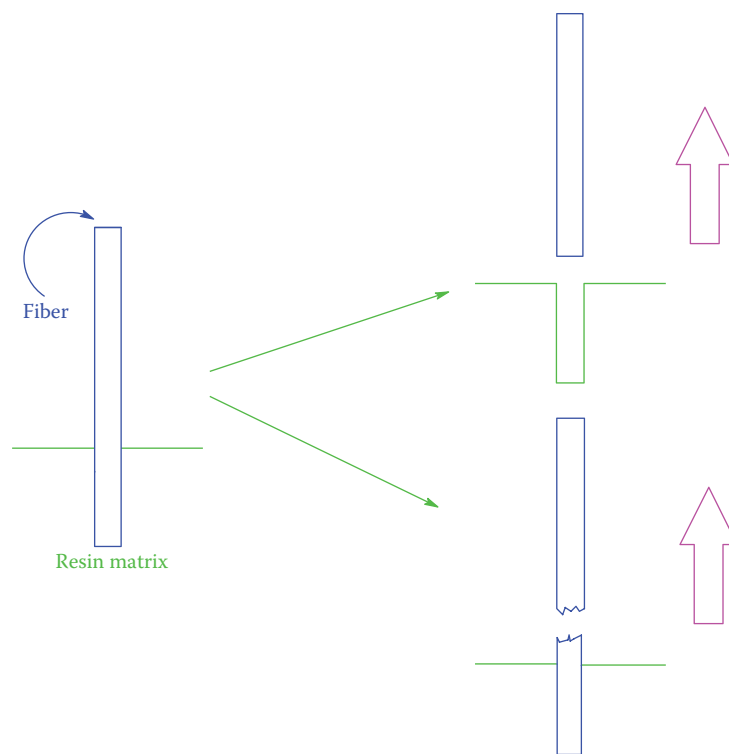


FIGURE 14.1 Tensile loading experiments performed on single fibers embedded in a matrix. The illustration on the left is preapplication of the tensile loading and those on the right are postapplication of the tensile loading.

the matrix–fiber composite becomes strong. The resin acts as a transfer agent, transferring and distributing applied stresses to the fibers. Generally, the fibers should have aspect ratios (ratio of length to diameter) exceeding 100, often much larger. Most fibers are thin (less than 20 μm thick, about a tenth the thickness of a human hair). Fibers should have a high tensile strength and most have a high stiffness, that is, low strain for high stress or little elongation as high forces are applied.

There exists a relationship between the “ideal” length of a fiber and the amount of adhesion between the matrix and the fiber. For instance, assume that only the tip, one end, of a fiber is placed in a resin (Figure 14.1, left). The fiber is pulled. The adhesion is insufficient to “hold” the fiber and it is pulled from the resin (Figure 14.1, top right). The experiment is repeated until the fiber is broken (outside the matrix) rather than being pulled (without breaking) from the resin (Figure 14.1, right bottom). Somewhere between the two extremes, there is a length where there exists a balance between the strength of the fiber and the adhesion between the fiber and matrix. Most modern composites utilize fiber/matrix combinations that exploit this “balance.”

Fiber failure is usually of the “catastrophic” type where the failure is sudden. This is typical in polymeric materials where the material is broken at the “weak link” and where the strength-related property is related to a combination of individual links (chains).

14.2.1 FIBERS AND RESINS

About 98% of the fibers employed in composites are glass (Section 10.5), carbon (graphite, carbon fibers, etc.; Sections 10.11 through 10.16), and aromatic nylons (often referred to as aramids; Section 5.7). Asbestos, a major fiber choice years ago, holds less than 1% of the market because of medical concerns linked to it.

Glass fibers are described using several terms including fiberglass, glass fibers, and fibrous glass. Glass fibers are mainly composed of silicon dioxide glass (Section 10.5). The glass fibers are

“pulled” from the glass melt forming fibers that range from 2 to 25 μm in diameter. The pulling action helps orientate the overall 3D structure giving a material with greater strength and stiffness along the axis of the pull. The ability to pull fibers from molten glass was known for centuries, but fibrous glass was not produced commercially until the 1930s.

As with many polymers, the limits of strength are due to the presence of voids. For glass fibers, these voids generally occur on the surface, thus care is taken to protect these surfaces through surface treatments with methacrylatochromic chloride, vinyl trichlorosilanes, and other silanes. These surface agents chemically react with the fiber surface acting to repel and protect the surface from harmful agents such as moisture.

A number of kinds of carbon-intense fibers are used, the most common being carbon and graphite fibers and carbon black. As in the case of fibrous glass, surface voids are present. Carbon-intense fibers are often surface treated with agents such as low molecular weight epoxy resins. Such surface treatments also aim at increasing the fiber–matrix adhesion.

Two general varieties of aromatic nylons are often employed. A less stiff variety is employed when some flexibility is important, while a stiffer variety is used for applications where greater strength is required. While good adhesion with the resin is often desired, poor adhesion is sometimes an advantage such as in the construction of body armor where “delamination” is a useful mode for absorbing an impact.

As we understand materials better, we are able to utilize them for additional applications. It is known that elongation flow through orifices can result in the stretching and reorientation of polymer chains giving a stronger fiber in the direction of pull. Some polymers become entangled and flow gives additional orientation. Finally, polymer solutions may be stable at rest, but under high rates of extrusion they may be removed from solution, forming a gel phase. These observations have allowed the production of a number of new polyolefin fibers including ultrahigh-modulus polyethylene fibers that are low density but relatively high tensile strength with an elongation at break over two times greater than glass and aromatic nylon fibers.

Both thermoset and thermoplastic resin systems are employed in the construction of composites. The most common thermoset resins are polyimides, unsaturated polyesters, epoxies, phenol-formaldehydes, and amino-formaldehydes. A wide variety of thermoplastic resins have been developed.

14.2.2 APPLICATIONS

Many of the applications for composite materials involve their (relative) light weight, resistance to weathering and chemicals, and their ability to be easily fabricated and machined. Bulk applications employ composites that are relatively inexpensive. Combinations of rigorous specifications, low volume, specific machining and fabrication specifications, and comparative price to alternative materials and solutions allow more expensive specialized composites to be developed and utilized.

Applications are increasing. Following is a brief description of some of these. One of the largest and oldest applications of composites is the construction of water-going vessels from rowboats, sailboats, racing boats, and motor craft to large seagoing ships. The use of freshwater- and salt water-resistant composites allowed the boating industry to grow and today includes a range from individually operated backyard construction to the use of large boatyards producing craft on an assembly line. Most of these craft are composed of fiberglass and fiberglass/carbon combination composites.

Compositions are also important in the construction of objects to both propel material into and material to exist in outer space. Because of the large amount of fuel required to propel spacecraft into outer space, weight reduction, offered by composites, is essential. The polymeric nature of composites also makes it an ideal material to resist degradation caused by the vacuum of outer space.

Many biomaterials are composites. Bone and skin are relatively light compared to metals. Composite structures can approach the densities of bone and skin and offer the necessary inertness and strength to act as body part substitutes.

Power-assisted arms have been made by placing hot-form strips of closed cell PE foam over the cast of an arm. Grooves are cut into these strips prior to application and carbon/resin added

to the grooves. The resulting product is strong and light and the cushioned PE strips soften the attachment site of the arm to the living body. Artificial legs can be fashioned in glass/polyester and filled with polyurethane foam adding strength to the thin-shelled glass/polyester shell. Artificial legs are also made from carbon/epoxy composite materials. Some of these contain a strong interior core with a soft, flexible “skin.”

Carbon/epoxy “plates” are now used in bone surgery replacing the titanium plates that had previously been employed. Usually a layer of connective tissue forms about the composite plate.

Rejection of composite materials typically does not occur, but as is the case for all biomaterials, compatibility is a major criterion. Often, lack of biocompatibility has been found to be the result of impurities (often additives) found in the materials. Removal of these impurities allows the use of the purified materials.

Carbon and carbon/glass composites are being used to make “advanced-material” fishing rods, bicycle frames, golf clubs, baseball bats, racquets, skis and ski poles, basketball backboards, etc. These come in one color—black—because the carbon fibers are black. Even so, they can be coated with about any color desired.

Composites are being employed in a number of automotive applications. These include racing car bodies and “regular” automobiles (Picture 14.1). Most automobiles have the lower exterior panels composed of rubbery, plastic blends, and/or composite materials. Other parts such as drive shafts and leaf springs in private cars and heavy trucks, antennas, and bumpers are being made from composite materials.

Industrial storage vessels, pipes, reaction vessels, and pumps are now made from composite materials. They offer needed resistance to corrosion, acids and bases, oils and gases, salt solutions, and the necessary strength and ease of fabrication to allow their continued adoption as a major industrial “building” material.

The Gulf War spotlighted the use of composite materials in the new age aircraft. The bodies of both the Stealth fighter and bomber are mainly carbon composites. The versatility is apparent when one realizes that the Gossamer Albatross, the first plane to cross the English Channel with human power, was largely made of composite materials including a carbon/epoxy and aromatic nylon composite body and propeller containing a carbon composite core.

The growth of composite materials in the aerospace industry is generally due to their outstanding strength and resistance to weathering and friction and their lightweight allowing fuel reduction savings. Its growth in commercial aircraft is seen in the increased use of fiberglass composite material in succeeding families of Boeing aircraft from about 20 yards² for the 707, to 200 yards² for the 727, to 300 yards² for the 737, and over 1000 yards² for the 747. This amount is increased in the Boeing 767 and includes other structural applications of other space-age composites. Thus, the Boeing 767 uses carbon/aromatic nylon/epoxy landing gear doors and wing-to-body fairings.



PICTURE 14.1 Author and his grandchild Herman V, in the author's sports car.

Until the late 1960s, almost all tactical aircraft were largely titanium. While titanium is relatively light, it is costly and has demanding production requirements so that its use was limited to moderate temperature aircraft applications. Today, most tactical aircraft have a sizable component that is polymeric, mainly composite. The Boeing F/A 18E/F and Lockheed F/A-22 have about 25%, by weight, composite material. It is projected that future military aircraft will have more than 35% composite materials.

Composites have displaced more conventional materials because they are lighter with greater strength and stiffness allowing them to carry a greater payload further. Composites are also relatively insensitive to flaws. Fatigue testing of composites show that they have a high resistance to cracking and fracture propagation compared to metals. They are stable and not subject to corrosion. However, in the design process, particular care must be taken with respect to the metal–composite interface because galvanic action of some metals will corrode when in contact with certain composites such as the carbon graphite/resin laminates.

The Stealth Bomber, more accurately known as the Northrop Grumman B-2 Spirit Stealth Bomber, is cited as the largest composite structure produced with more than 30% of the weight being carbon graphite epoxy composites. The Stealth Bomber was originally slated to hunt Russian mobile missiles that were built in the 1980s. It was deployed in 1993 and has a wingspan of over 52 m, a 21 m length, and is over 5 m high. The reported cost of a single B-2 is varied ranging from about \$2.4 billion to a low of \$500 million. In any case, it is expensive and only about 21 have been produced with no plans to build more. The technology associated with the B-2 has been continuously upgraded allowing it to perform tasks with even greater accuracy and stealthiness.

The word stealth comes from ancient roots meaning “to steal.” There are a number of stealth aircraft in operation today with others coming on line. To be “stealthy,” a plane should

- Be difficult to see with the eye
- Make little or no noise (achieved by muffling the engines)
- Display little heat from engines and other moving parts
- Minimize a production of contrails and other signs
- Absorb and scatter radar beams

The most common mode of aircraft detection is radar. Essentially, radar is the detection of radio waves that have been “thrown out” and that bounce off objects returning to the site of origin. Today’s radar, if properly used, can help identify the location, speed, and identity of the aircraft. The radar cross section (RCS) of an aircraft is how much echo the plane sends from radar. Birds have an RCS of about 0.01 m². The Stealth Bomber has an RCS of 0.75 m². The Stealth Bomber, and many stealth aircraft, gain their “stealthiness” from mainly both the shape of the aircraft and the presence of radar absorbing material (RAM). The RAM is made to absorb and eliminate radio waves rather than reflecting them. Most of the RAM materials are polymeric.

The Stealth Bomber has a covering of RAM skin. The basic elements of the composite covering consist of graphite carbon fibers embedded in an epoxy resin. The carbon fibers dissipate some of the absorbed radiation by ohmic heating. The material also contains ferrite particles that are important because they are good “lousy” radar absorbers. The good absorbency of radar signals is dependent on a low dielectric constant. In principle, thicker coatings increase absorption of signals. Thick coatings increase cost and weight and decrease the aerodynamics of the aircraft. (In truth, the flying wing is aerodynamically unstable and is flown with a quadruple-redundant fly-by-wire, FBW, system.) The thickness of the layers needed to provide the necessary radar signature can be reduced through the use of materials with intermediate absorption behavior, the ferrite particles, to smooth the interference between the aircraft and the surrounding air since extreme differences causes strong radar reflections.

The graphite resin layers are laid similar to making the hull of a fiberglass boat hull. This layering, over a frame or mold, is accomplished using computer-guided assistance. Thin layers of gold foil are also applied to the canopy to give radar reflecting characteristics similar to the rest of the aircraft.

The Stealth Bomber is shaped like a wafer-thin Batman boomerang with smooth, knife-like curved surfaces that lack right angles. The reflective nature of the design can be understood by considering looking straight on at a mirror. Your image will be reflected back at you. Tilt the

mirror 45° and it will reflect your image upward. The bomber design is a large system of triangles with flat surfaces angled to deflect radar waves away from the radar emitter. It scrambles the radar all about but not back to the receiver. This shape is also intended to offer a minimum of disruption to the air, that is, the shape brings about a minimum amount of air resistance giving a minimization of radar difference between the aircraft and its surroundings.

The use of composites allows few seams to be present reducing radar reflections. For years, seams were believed necessary for large aircraft. For instance, the wings of the large bombers actually “flap” in the wind contributing to the ability of the aircraft to remain in the air for long periods of time. Without seams and some flexibility these large metal-based aircraft would literally snap apart. Composite assemblies have a minimum of flexibility. To discourage reflections in unwanted directions, the electrical continuity is maintained over the entire surface of the bomber. Thus, all moving and major body parts are tight fitting. The composite nature of the outer skin allows this to be closely achieved.

The engines are buried deep within the aircraft’s interior reducing noise and “heat signature.” The heat signature is further reduced by mixing the jet’s exhaust with cooled air and exiting it through slit-like vents.

Stealth aircraft are often painted a medium gray or bluish gray that matches the sky so that it does not stand out. Coatings are composed of RAM that penetrates into cracks reducing the number of minor repairs and use of special tape for repair. Every screw, panel, seam, and gap is covered with a special tape or the RAM coating adding to the bomber’s stealthiness.

Because most traditional polymers have low dielectric constants, they can be used as RAMs and many have been used in various applications in military and civil applications. While the B-2 largely depends on a graphite carbon impregnated composite for its integrity and stealthiness, many other polymers are used as RAMs. Many of these are various elastomeric materials. Neoprene is widely used in naval applications as a RAM because of its good weather resistance. Nitrile is used for fuel and oil resistance and fluoroelastomers are used where wide temperature ranges are encountered. Often, thin flexible sheets or layers of the elastomer are adhered to a metal substrate. While the polysiloxanes offer good RAM behavior, they are difficult to adhere to many metal structures and thus are not as widely employed in comparison to neoprene and nitrile rubbers. Products are also made using various molding methods. To improve weather resistance, the absorber is often painted with another RAM, an epoxy or urethane-based coating.

14.3 NANOCOMPOSITES

Nature has employed nanomaterials since the beginning of time. Much of the inorganic part of our soil is a nanomaterial with the ability to filter out particles often on a molecular or nano level. The driving force toward many of the nanomaterials is that they can offer new properties or enhanced properties unobtainable with the so-called traditional bulk materials. Along with lightweight, high strength to weight features, and small size, new properties may emerge because of the very high surface area to mass where surface atomic and molecular interactions become critical. The nano world is often defined for materials where some dimension is on the order of 1–100 nm. In a real way, single linear polymers are nanomaterials since the diameter of the single chain is within this range. The carbon–carbon bond length is on the order of 0.15 nm or the average zigzag bond length is about 0.13 nm. While some short to moderate-length vinyl polymers have contour lengths less than 100 nm, higher-molecular-weight polymers have contour lengths that far exceed this. Even so, individual polymer chains fall within the realm of nanomaterials when they act independently. Since the cumulative attractive forces between chains are large, polymer chains generally act in concert with other polymer chains leading to properties that are dependent on the bulk material. Chain folding, inexact coupling, chain branching are some of the reasons that bulk properties fall short of theoretical properties, but with the ability to work with chains individually, strength and related properties are approaching theoretical values. Much of the nanorevolution with materials involves how to synthesize and treat materials on an individual basis as well as visualizing uses for these materials.

The ultimate strength and properties of many materials is dependent upon the intimate contact between the various members. Thus, for ceramics, nanosized particles allow a more homogeneous structure resulting in stronger ceramic materials.

Nanocomposites have also been with us since almost the beginning of time. Our bones are examples of nanocomposites. The reinforcement material is platelike crystals of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, with a continuous phase of collagen fibers. The shell of a mollusk is microlaminated containing as the reinforcement aragonite (a crystalline form of calcium carbonate) and the matrix is a rubbery material. Allowing nature to be a source of ideas is a continuing theme in synthetic polymer science, including modification of natural polymers. Much of the renewed interest in nano composite materials is the direct result of the availability of new nanobuilding blocks.

Within a composite material, much of the ultimate strength comes from the intimate contact the fiber has with the matrix material. Nanofibers allow more contact between the fiber (on a weight basis) and the matrix resulting in a stronger composite because of an increased fiber surface–matrix interface.

A number of inorganic/organic nanocomposites have been made. These include nanoinorganics including nanofibers from silicon nitride, titanium(IV) oxide, zirconia, alumina, titanium carbide, and tungsten carbide. It also includes the use of special clays (layered silicates) mixed with nylons to form nanocomposites. The clay layers are separated giving platelets about 1 nm thick. These nylon–clay microcomposites are used to make the air intake cover of some of the Toyota automobiles. These individual clay platelets have also been used to form nearly single layer polymer chain sheets similar to lignin. The interaction with the silicate surface encourages the polymer chains to take different arrangements. To be effective, the hydrophilic silicate surface is generally modified to accommodate the more hydrophobic common monomers and polymers.

While carbon fiber (thickness on the order of 1000 nm) composites offer very strong materials, carbon nanotubes make even stronger composites (Picture 14.2). These carbon nanotubes have aspect ratios of over 1000 (ratio of length to diameter). Further, because some carbon nanotubes are electrically conductive, composites containing them can be made to be conductive. A number of carbon nanotube matrices have been made including using a number of engineering resins such as polyesters, nylons, polycarbonates, and poly(phenylene ether).

Individual polymer chains can be more flexible than groups of chains (bulk) even when the polymer is generally considered to be rigid. This is presumably because single chains have less torsional strain imparted by near neighbors and various chain entanglements and associations are not present. Compared with carbon fibers, carbon nanotubes imbedded within a polymer



PICTURE 14.2 This is a newer sports car of the author's that incorporates carbon fibers and nanotubes as building materials.

matrix can withstand much greater deformations before they break. Further, nanomaterials are generally more efficient in transferring applied load from the nanomaterial to the matrix. These factors contribute to the greater strength of carbon nanotube composites.

As noted before, adhesion between the reinforcing agent and matrix is important. Some matrix materials do not adhere well with certain fibers. This is partially overcome through introduction of defects or functional groups onto the nanomaterials that act as hooks to anchor them to the matrix material.

14.4 PLASTICIZERS

Flexibilizing of polymers can be achieved through internal and external plasticization. Internal plasticization can be produced through copolymerization giving a more flexible polymer backbone or by grafting another polymer onto a given polymer backbone. Thus, poly(vinylchloride-co-vinyl acetate) is internally plasticized because of the increased flexibility brought about by the change in structure of the polymer chain. The presence of bulky groups on the polymer chain increases segmental motion and placement of such groups through grafting acts as an internal plasticizer. Internal plasticization achieves its end goal at least in part through discouraging association between polymer chains. However, grafted linear groups with more than 10 carbon atoms can reduce flexibility because of side-chain crystallization when the groups are regularly spaced.

External plasticization is achieved through incorporation of a plasticizing agent into a polymer through mixing and/or heating. The remainder of this section focuses on external plasticization.

Plasticizers should be relatively nonvolatile, nonmobile, inert, inexpensive, nontoxic, and compatible with the system to be plasticized. They can be divided based on their solvating power and compatibility. Primary plasticizers are used as either the sole plasticizer or the major plasticizer with the effect of being compatible with some solvating nature. Secondary plasticizers are materials that are generally blended with a primary plasticizer to improve some performance, such as flame resistance and mildew resistance, or to reduce cost. The division between primary and secondary plasticizers is at times arbitrary. Here we will deal with primary plasticizers.

According to the ASTM D-883 definition, a plasticizer is a material incorporated into a plastic to increase its workability and flexibility or dispensability. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and T_g . The plasticizers market accounts for yearly sales of about 8 million tons.

Waldo Semon patented the use of tricresyl phosphate as a plasticizer for PVC in 1933. This was later replaced by the less toxic di-2-ethylhexyl phthalate (DOP), which is now the most widely used plasticizer. Volume wise, about 90% of the plasticizers are used with PVC and PVC-containing systems.

The effect of plasticizers has been explained by the lubricity, gel, and free volume theories. The lubricity theory states that the plasticizer acts as an internal lubricant and permits the polymers to slip past one another. The gel theory, which is applicable to amorphous polymers, assumes that a polymer, such as PVC, has many intermolecular attractions that are weakened by the presence of a plasticizer. In free volume theories, it is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at T_g . There may be some truth in most of these theories. It is believed that a good plasticizer solubilizes segments allowing them some degree of mobility creating free volume through Brownian movement. In turn, this lowers the temperature where segmental mobility can occur making the material more flexible.

Most plasticizers are classified as being general purpose, performance, or specialty plasticizers. General purpose plasticizers are those that offer good performance inexpensively. Most plasticizers are of this grouping. Performance plasticizers offer added performance over general purpose plasticizers generally with added cost. Performance plasticizers include fast-solvating materials such as butyl benzyl phthalate and dihexyl phthalate, low-temperature plasticizers such as di-*n*-undecyl phthalate and di-2-ethylhexyl adipate, and the so-called permanent plasticizers such as tri-2-ethylhexyl trimellitate, triisononyl trimellitate, and diisodecyl phthalate. Specialty plasticizers include materials that provide important properties such as reduced migration, improved stress-strain behavior, flame resistance, and increased stabilization.

TABLE 14.2 Solubility Parameters of Typical Plasticizers

Plasticizer	Solubility Parameter (H)
Paraffinic oils	7.5
Dioctyl phthalate	7.9
Dibutoxyethyl phthalate	8.0
Tricresyl phosphate	8.4
Dioctyl sebacate	8.6
Triphenyl phosphate	8.6
Dihexyl phthalate	8.9
Hydrogenated terphenyl	9.0
Dibutyl sebacate	9.2
Dibutyl phthalate	9.3
Dipropyl phthalate	9.7
Diethyl phthalate	10.0
Glycerol	16.5

The three main chemical groups of plasticizers are phthalate esters, trimellitate esters, and adipate esters. In all three cases, performance is varied through the introduction of different alcohols into the final plasticizer product. There is a balance between compatibility and migration. Generally, the larger the ester grouping, the less the migration up to a point where compatibility becomes a problem and where compatibility now becomes the limiting factor.

Compatibility is the ability to mix together without forming different phases. A good approach to measure the likelihood of compatibility is solubility parameters (Section 3.2). Plasticizers with solubility parameters and type of bonding similar to those of the polymer are more apt to be compatible than when the solubility parameters are different. The solubility parameter for PVC (9.66) is near that of good plasticizers for PVC such as DOP (8.85). Table 14.2 contains solubility parameters for typical plasticizers.

The development of plasticizers has been plagued with toxicity problems. Thus, the use of highly toxic polychlorinated biphenyls (PCBs) has been discontinued. Phthalic acid esters, such as DOP, may be extracted from blood stored in plasticized PVC blood bags and tubing. These aromatic esters are also distilled from PVC upholstery in closed automobiles in hot weather. These problems have been solved by using oligomeric polyesters as nonmigrating plasticizers in place of DOP for appropriate situations. Recently, some limited tests have indicated a relationship of prenatal exposure to phthalates and reproductive abnormalities in male babies. The chemical industry is monitoring these results taking appropriate steps to limit or eliminate exposure to dangerous materials.

Experimental investigations and assessments show that the average person takes in about 2 g a year of external plasticizers. Most of this is from traces of di-(2-ethylhexyl) adipate (DOA) migrating from food packaging. The so-called no observed effect level for DOA in rodents is about 40 mg per kg of body weight per day. Extrapolation for a person equates to 1000 g of plasticizer for a “safety factor” of about 500. Even so, increased efforts to evaluate the safety of plasticizers continue. Phthalates account for about 70%–80% of the plasticizers used. Vinyl products, that is, ones made from poly(vinyl chloride), are the largest users of plasticizers. Products containing them are everywhere.

Plasticizers extend the lower temperature range for use of materials since they discourage polymer chain associative behavior and encourage segmental flexibility increasing the rotational freedom effectively decreasing the materials typical T_g .

When present in small amounts, plasticizers can act as antiplasticizers increasing the hardness and decreasing the elongation of the material partly due to their ability to fill voids. Inefficient plasticizers require larger amounts of plasticizers to overcome the initial antiplasticization. However, good plasticizers such as DOP change from being antiplasticizers to plasticizers when less than 10% of the plasticizer is added to PVC.

External plasticizers are not permanent. Plasticizer molecules associate with one another eventually creating “preferred” migration routes to the material’s surface where the plasticizer is

rubbed or washed away. The preferential association of plasticizers also leaves some sites less flexible and creates variations in the material's stress-strain and expansion-contraction behaviors.

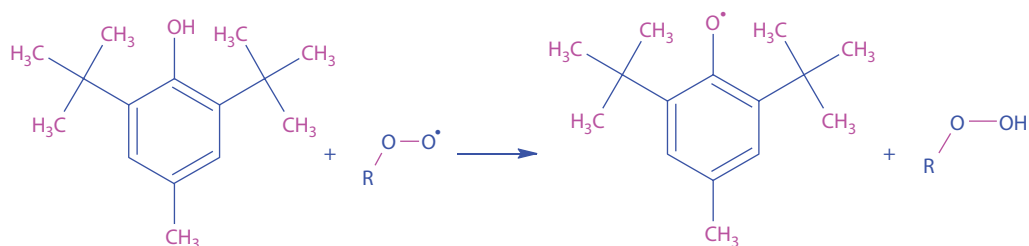
As noted elsewhere in this text, the health issues related to plasticizers is an issue particularly with respect to their use in materials that come in contact with our food. While the leachability of most plasticizers is small, it is real and ppm to ppt amounts of some plasticizers have been found to leach to the surfaces of food packaging materials. Thus, efforts are aimed at lowering to near zero the migration of plasticizers to surfaces as well as using safe plasticizers so that even when migration occurs, the health effects are near zero.

14.5 ANTIOXIDANTS

Antioxidants retard oxidative degradation. Heat, mechanical shear, and ultraviolet (UV) radiation can be responsible for the formation of free radicals, which in turn can act to shorten polymer chains and increase cross-linking, both leading to a deterioration in material properties. Free radical production often begins a chain reaction. Primary antioxidants donate active hydrogen atoms to free radical sites thereby quenching or stopping the chain reaction. Secondary antioxidants or synergists act to decompose free radicals to more stable products.

Polymers such as polypropylene (PP) are not usable outdoors without appropriate stabilizers because of the presence of readily removable hydrogen atoms on the tertiary carbon atoms. PP and many other polymers are attacked during precessing or outdoor use in the absence of stabilizers because of chain degradation reactions. These degradation reactions are retarded by the presence of small amounts of antioxidants. Naturally occurring antioxidants are present in many plants and trees such as the *Hevea* rubber trees. The first synthetic antioxidants were synthesized independently by Caldwell and by Winkelman and Gray by the condensation of aromatic amines with aliphatic aldehydes.

Many naturally occurring antioxidants are derivatives of phenol and hindered phenols, such as di-*tert*-butyl paracresol (14.2). It has the ability to act as a chain transfer agent forming a stable free radical that does not initiate chain radical degradation. However, the phenoxy free radical may react with other free radicals producing quinone derivatives.



(14.2)

Since carbon black has many stable free radicals, it may be added to polymers such as polyolefins to retard free radical formation by attracting and absorbing other free radicals. It is customary to add small amounts of other antioxidants to enhance the stabilization by a "synergistic effect" whereby many antioxidant combinations are more stable than using only one antioxidant.

14.6 HEAT STABILIZERS

Heat stabilizers are added to materials to impart protection against heat-induced decomposition. Such stabilizers are needed to protect a material when it is subjected to a thermal-intense process (such as melt extrusion) or when the material is employed under conditions where increased heat stability is needed.

In addition to the free radical chain degradation described for polyolefins, other types of degradation occur including dehydrohalogenation that occurs for PVC. When heated, PVC may lose

hydrogen chloride forming chromophoric conjugated polyene structures eventually yielding fused aromatic ring systems (14.3).

This type of degradation is accelerated in the presence of iron salts, oxygen, and hydrogen chloride. Toxic lead and barium and cadmium salts act as scavengers for hydrogen chloride and may be used for some applications such as wire coating. Mixtures of magnesium and calcium stearates are less toxic and effective. Among the most widely used heat stabilizers for PVC are the organotin products. Many of these are based on organotin polymers discovered by Carraher.



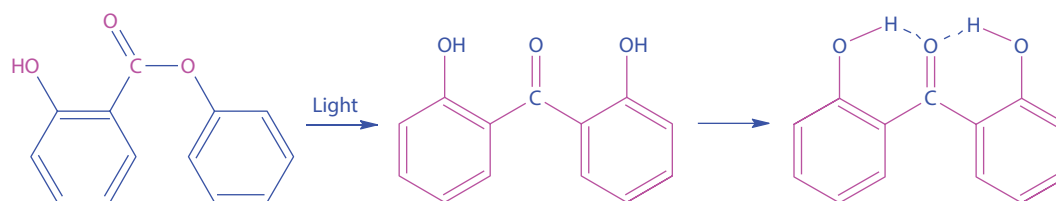
(14.3)

14.7 ULTRAVIOLET STABILIZERS

UV stabilizers act to quench UV radiation. While much of the sun's high-energy radiation is absorbed by the atmosphere, some radiation in the 280–400 nm (UV) range reaches the Earth's surface. Since the energy of this radiation is on the order of 70–100 kcal/mol (280–400 kJ/mol), UV radiation is sufficient to break many chemical bonds and thus cause polymer chains to break. This breakage generally does one of two things: (1) it can increase the amount of cross-linking through subsequent formation of bonds after the initial bond breakage, or (2) bond breakage can result in a decreased chain length. Either of these results in a decreased overall strength of the polymeric material and often the yellowing of many organic polymers. Cross-linking also results in the embrittlement of these polymers.

PE, PVC, PS, PET, and PP are degraded at wavelengths of 300, 310, 319, 325, and 370 nm, respectively. The bond energy required to cleave the tertiary carbon hydrogen bond in PP is only 320 kJ/mol that corresponds to a wavelength of 318 nm.

Since the effect of UV radiation on synthetic polymers is similar to its effect on the human skin, it is not surprising that UV stabilizers such as phenyl salicylate have been used for commercial polymers and in suntanning lotions for many years. Phenyl salicylate rearranges in the presence of UV radiation forming 2,2'-dihydroxybenzophenone (14.4). The latter and other 2-hydroxybenzophenones act as energy transfer agents, that is, they absorb energy forming chelates that release energy at longer wavelengths by the formation of quinone derivatives.



(14.4)

Over 100,000 tons of UV stabilizers are used by the U.S. polymer industry annually.

14.8 FLAME RETARDANTS

Flame retardants inhibit or resist the ignition and spread of fire. There are several general types of flame retardants that have been added to synthetic polymers. These include synthetic materials generally halocarbons and phosphorus-containing materials. Another class of flame retardants is minerals such as aluminum hydroxide, boron compounds, magnesium hydroxide, and antimony trioxide. Many of these present health problems. This includes most of the halocarbons such as PCBs.

In general, flame retardants resist fire by several mechanisms. Some, such as magnesium hydroxide and aluminum hydroxide decompose when exposed to fire through endothermic means removing heat from the fire. Inert fillers such as calcium carbonate and talc dilute the portion of material that can burn. Thus, a home made of concrete block is less apt to burn completely than a home that is made of wood since concrete block reduces the amount of flammable material.

While some polymers such as PVC are not readily ignited, most organic polymers, like hydrocarbons, will burn. Some will support combustion, such as polyolefins, SBR, wood, and paper, when lit with a match or some other source of flame. The major products for much of this combustion are carbon dioxide (or carbon monoxide if insufficient oxygen is present) and water.

Since many polymers are used as shelter and clothing and in household furnishing, it is essential that they have good flame resistance. Combustion is a chain reaction that may be initiated and propagated by free radicals. Since halides and phosphorus radicals couple with free radicals produced in combustion terminating the reaction, many flame retardant are halide (halogen) or phosphorus-containing compounds. These may be additives; external retardants sprayed onto the material such as antimony oxide and organic bromides or internal retardants such as tetra-bromophthalic anhydride that are introduced during the polymerization process so that they are part of the polymer chain.

Fuel, oxygen, and high temperature are essential for the combustion process. Thus, polyfluorocarbons, phosphazenes, and some composites are flame resistant because they are not good fuels. Fillers such as alumina trihydrate release water when heated and hence reduce the temperature of the combustion process. Compounds such as sodium carbonate, which releases carbon dioxide when heated, shield the reactants from oxygen. Char, formed in some combustion processes, also shields the reactants from a ready source of oxygen and retard the outward diffusion of volatile combustible products. Aromatic polymers, such as PS, tend to char and some phosphorus and boron compounds catalyze char formation aiding in controlling the combustion process.

Synergistic flame retardants such as a mixture of antimony trioxide and an organic bromo compound are more effective than single flame retardants. Thus, mixtures are often employed to protect materials and people.

Since combustion is subject to many variables, tests for flame retardancy may not correctly predict flame resistance under unusual conditions. Thus, a disclaimer stating that flame retardancy tests do not predict performance in an actual fire and must accompany all flame-retardant products. Flame retardants, like many organic compounds, may be toxic or may produce toxic gases when burned. Hence, care must be exercised with using fabrics or other polymers treated with flame retardants.

14.9 COLORANTS

Color is a subjective phenomenon whose esthetic value has been recognized for centuries. Since it is dependent on the light source, the object, and the observer, color is not subject to direct measurement, though instruments can measure a color for reproducibility. Colorants that provide color in polymers may be soluble dyes or comminuted pigments.

Some polymeric objects, such as rubber tires, are black because of the presence of high proportions of carbon black filler. Many other products, including some paints, are white because of the presence of titanium dioxide (titanium(IV) oxide), the most widely used inorganic pigment. More than 50,000 tons of colorants are used annually by the polymer industry.

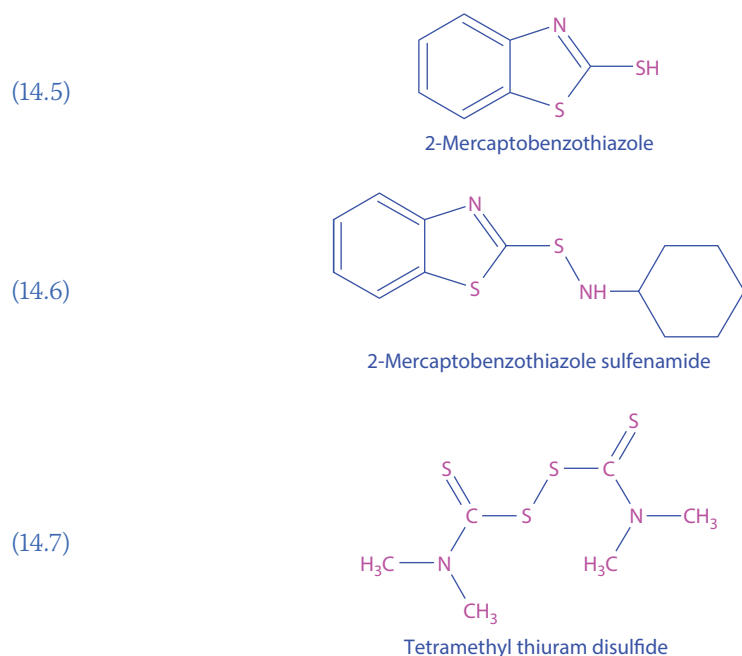
Pigments are classified as organic or inorganic. Organic pigments are brighter, less dense, and smaller in particle size than the more widely used, more opaque inorganic colorants. Iron oxides or ochers are available as yellow, red, black, brown, and tan.

Carbon black is the most widely used organic pigment, but phthalocyanine blues and greens are available in many shades and are also widely used.

14.10 CURING AGENTS

The use of curing agents began with the serendipitous discovery of vulcanization of *Hevea* rubber with sulfur by Charles Goodyear in 1838. The conversion of an A- or B-stage phenolic novolac resin with hexamethylenetetramine in the early 1900s was another relatively early use of curing (cross-linking) agents. Organic accelerators, or catalysts, for the sulfur vulcanization of rubber were discovered by Oenslager in 1912. While these accelerators are not completely innocuous, they are less toxic than aniline, used prior to the discovery of accelerators. Other widely used accelerators are thiocarbonyl and 2-mercaptobenzothiazole (Captax).

Captax (Structure 14.5) is used to the extent of 1% with *Hevea* rubber and accounts for the major part of the more than 30,000 tons of accelerators used annually in the United States. Other accelerators widely used include 2-mercaptobenzothiazole sulfonamide (Santocure; Structure 14.6), used for the vulcanization of SBR, dithiocarbamates, and thiuram disulfides. Thiuram disulfide (Structure 14.7) is a member of a group called ultra-accelerators that allow the curing of rubber at moderate temperatures and may be used in the absence of sulfur.



Initiators such as benzoyl peroxide are used not only for the initiation of chain reaction polymerization but also for the curing of polyesters and ethylene–propylene copolymers and for the grafting of styrene on elastomeric polymer chains.

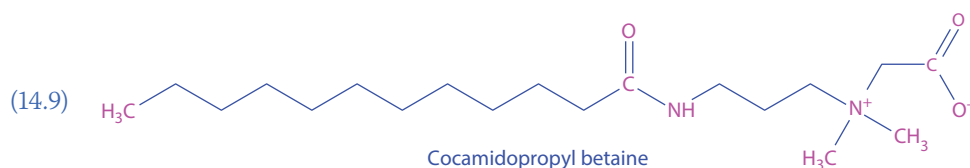
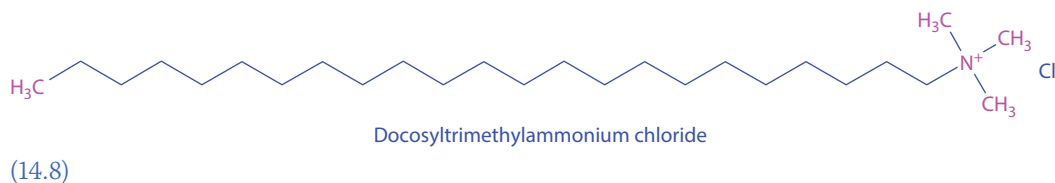
Unsaturated polymers such as alkyd resins can be cured or “dried” in the presence of oxygen, a heavy metal, and an organic acid called a drier. The most common organic acids are linoleic, abietic, naphthenic, octoic, and tall oil fatty acids.

14.11 ANTISTATIC AGENTS: ANTISTATS

Antistatic agents (antistats) dissipate static electrical charges. Insulating materials, including most organic plastics, fibers, films and elastomers, can build up electrical charge. Because these largely organic materials are insulators, they are not able to dissipate the charge. Such charge buildup is particularly noticeable in cold, dry climates and leads to dust attraction and sparking.

Antistatic agents can be either internal or external. External antistats are applied to the surface by wiping, spraying, etc. These surface treatments act to prevent static charge buildup. Internal antistats are added during the processing and become an integral part of the bulk composition

of the material. Because surface treatments are often worn away through washing, waxing, and handling, the external antistats must be replenished. Internal antistats are added to allow the antistats to come (“bleed”) to the surface over a long time, giving the material long-term protection. Many antistatic agents are long-chain aliphatic amines and amides, esters of phosphoric acid, poly(ethylene glycol) esters, PEGs, and quaternary ammonium salts such as docosyltrimethylammonium chloride (14.8) or cocamidopropyl betaine (14.9).



Antistatic agents often have both a hydrophobic (above the hydrocarbon chain; 14.8, 14.9) and a hydrophilic (salts, quaternary amine, amide; 14.8, 14.9) portion. The hydrophobic portion is attracted to the hydrophobic part of most vinyl polymers, while the hydrophilic portion interacts with the moisture in the air.

14.12 CHEMICAL BLOWING AGENTS

Chemical blowing agents (CBAs) are employed to create lighter weight material through formation of a foam. Physical CBAs are volatile liquids and gases that expand and volatilize during processing through control of the pressure and temperature.

Cellular polymers not only provide insulation and resiliency but are usually stronger on a weight basis than solid polymers. Fluid polymers may be foamed by the addition of low-boiling liquids such as pentane or fluorocarbons by blowing with compressed nitrogen gas, by mechanical heating, and by the addition of foaming agents. While some carbon dioxide is produced when polyurethanes are produced in the presence of moisture, auxiliary propellants are also added to the prepolymer mixture to give the desired amount of foaming. The most widely used foaming agents are nitrogen-producing compounds such as azobisformamide. Other foaming agents that decompose at various temperatures are available.

14.13 COMPATIBILIZERS

Compatibilizers are compounds that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible yielding a homogeneous product that does not separate into its components. Typically, compatibilizers act to reduce the interfacial tension and are concentrated at phase boundaries. Reactive compatibilizers chemically react with the materials they are to make compatible. Nonreactive compatibilizers perform their task by physically making the various component materials compatible.

14.14 IMPACT MODIFIERS

Impact modifiers improve the resistance of materials to stress. Most impact modifiers are elastomers such as ABS, BS, methacrylate–butadiene–styrene, acrylic, ethylene–vinyl acetate, and chlorinated polyethylene.

14.15 PROCESSING AIDS

Processing aids are added to improve the processing characteristics of a material. They may increase the rheological and mechanical properties of a melted material. Acrylate copolymers are often utilized as processing aids.

14.16 LUBRICANTS

Lubricants are added to improve the flow characteristics of a material during its processing. They operate by reducing the melt viscosity or by decreasing adhesion between the metallic surfaces of the processing equipment and the material being processed. Internal lubricants reduce molecular friction consequently decreasing the material's melt viscosity allowing it to flow more easily. External lubricants act by increasing the flow of the material by decreasing the friction of the melted material as it comes in contact with surrounding surfaces. In reality, lubricants such as waxes, amides, esters, acids, and metallic stearates act as both external and internal lubricants.

14.17 MICROORGANISM INHIBITORS

While most synthetic polymers are not directly attacked by microorganisms such as fungi, yeast, and bacteria, they often allow growth on their surfaces. Further, naturally occurring polymeric materials such as cellulose, starch, protein, and vegetable oil-based coatings are often subject to microbiologic deterioration. Finally, some synthetics that contain linkages that can be “recognized” by natural enzymes (such as amide and ester linkages) may also be susceptible to attack.

One major antimicrobial grouping once was organotin-containing compounds. These monomeric organotin-containing compounds are now outlawed because of the high “leaching” rates of these material affecting surrounding areas. Even so, polymeric versions are acceptable and can be considered “nonleaching” or slowly leaching.

Organic fungistatic and bacteriostatic additives are currently employed, but in all cases, formation of resistant strains and the toxicity of the bioactive additive must be considered.

SUMMARY

1. Most polymers contain materials added to modify some chemical and/or physical property that allows them to better fulfill their intended use. These added materials are called additives.
2. Fillers are relatively inert materials that usually add bulk but when well chosen, they can enhance physical and chemical properties. Many natural and synthetic materials are used as fillers today. These include polysaccharides (cellulose), lignin, carbon-based materials, glass, and other inorganic materials.
3. The most important reinforced materials are composites. Composites contain strong fibers embedded in a continuous phase. They form the basis of many of the advanced and space-age products. They are important because they offer strength with relatively low weight and good resistance to weathering. Typical fibers are fibrous glass, carbon-based, aromatic nylons, and polyolefins. Typical resins are polyimides, polyesters, epoxies, phenol-formaldehyde, and many other synthetic polymers. Applications include biomedical, boating, aerospace and outer space, sports, automotive, and industry.
4. Nanocomposites employ nanofibers that allow for much greater fiber–resin surface contact per mass of fiber, and consequently, they generally offer greater strength in comparison to similar non-nanocomposites.
5. Plasticizers allow polymer chains to move past one another allowing wholesale flexibility. They can enhance flexibility above and below the glass transition temperature of

- a polymer. Plasticization can occur through addition of an external chemical agent or may be incorporated within the polymer itself.
6. Antioxidants retard oxidative degradation.
 7. Heat stabilizers allow some protection to heat-induced decomposition.
 8. UV stabilizers act to quench UV radiation. UV radiation is strong enough to break chemical bonds and thus cause polymer chains to break either increasing the amount of cross-linking through subsequent formation of bonds or can result in a decreased chain length. Either of these results in a decreased overall strength of the polymeric material.
 9. Flame retardants impart to the polymers some ability to resist ready combustion. Since fuel, oxygen, and high temperature are essential for the combustion of polymers, the removal of any of these prerequisites retards combustion. Flame retardants act through a variety of mechanisms including char formation, combination with free radical species that promote further combustion, and through release of water.
 10. A variety of inorganic and organic compounds are used to color polymers.
 11. The rate of cross-linking of polymers, such as natural rubber, is increased through the use of accelerators, often misnamed as catalysts.
 12. Antistats reduce the electrostatic charge on the surface of polymers,
 13. Gas-producing additives are essential for the formation of cellular products such as foam cushions.
 14. Biocides are used to prevent or retard attack on polymers by microorganisms.
 15. Lubricants serve as processing aids that discourage the sticking of polymers to metal surfaces during processing.
 16. Other important additives are coloring agents, curing agents, antistatic agents, CBAs, and microorganism inhibitors.
 17. Each of these additives perform a critical role in allowing polymers to be processed and utilized giving the variety of useful products we have today.

GLOSSARY

Accelerator: Catalyst for the vulcanization of rubber.

Acicular: Needle-shaped.

Antioxidant: Additive that retards polymer degradation by oxidative modes.

Antiplasticization: Hardening and stiffening effect observed when small amounts of a plasticizer are added to a polymer.

Antistat: Additive that reduces static charges on polymers.

Aspect ratio: Ratio of length to diameter.

Biocide: Additive that retards attack by microorganisms.

Blocking: Sticking of sheets of film to one another.

Bound rubber: Rubber adsorbed on carbon black and that is insoluble in benzene.

Bulk molding compound (BMC): Resin-impregnated bundles of fibers.

Carbon black: Finely divided carbon made by the incomplete combustion of hydrocarbons.

Cellular polymers: Foams.

Chemical blowing agent: Volatile liquids and gases that expand and/or volatilize during processing of a material creating pockets leading to lighter weight materials.

Colorant: Color causing material; usually a dye or pigment.

Comminuted: Finely divided.

Compatibilizers: Chemicals that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible, giving a more homogeneous material.

Composites: Materials that often contain strong fibers embedded in a continuous phase called a matrix or resin.

Continuous phase: Resin in a composite.

Coupling agents: Products that improve the interfacial bond between the filler and resin.

Curing agent: Additive that causes cross-linking.

Diatomaceous earth: Siliceous skeletons of diatoms.

Discontinuous phase: Discrete filler additive, such as fibers, in a composite.

- Drier:** Catalyst that aids the reaction of polymers with oxygen.
- Drying:** Cross-linking of an unsaturated polymer chain.
- Energy transfer agent:** Molecule that absorbs high energy and reradiates it in the form of lower energy.
- Extender:** Term sometimes applied to an inexpensive filler.
- Fiberglass:** Trade name for fibrous glass.
- Fibrous filler:** Fiber with an aspect ratio of at least 100:1.
- Fibrous glass:** Filaments made from molten glass.
- Filament winding:** Process in which resin-impregnated continuous filaments are wound on a mandrel and the composite is cured.
- Filler:** Usually a relatively inert material used as the discontinuous additive; generally inexpensive.
- Flame retardant:** Additive that increases the flame resistance of a polymer.
- Foaming agent:** Gas producer.
- Free volume:** Volume not occupied by polymer chains.
- Fuller's earth:** Diatomaceous earth.
- Gel theory:** Theory that assumes that in the presence of a pseudo-three-dimensional structure intermolecular attractions are weakened by the presence of a plasticizer.
- Graphite fibers:** Fibers made by the pyrolysis of polyacrylonitrile fibers.
- Heat stabilizers:** Additives that retard the decomposition of polymers at elevated temperatures.
- Impact modifiers:** Materials that improve the resistance of materials to stress.
- Lamellar:** Sheetlike.
- Laminate:** Composite consisting of layers adhered by a resin.
- Low-profile resins:** Finely divided incompatible resins that made a rough surface smooth.
- Lubricants:** Materials that improve the flow characteristics of materials, generally during processing.
- Lubricity theory:** Theory that plasticization occurs because of increased polymer chain slippage.
- Mica:** Naturally occurring lamellar silicate.
- Microballoons:** Hollow glass spheres.
- Mold release agent:** Lubricant that prevents polymers from sticking to mold cavities.
- Novaculite:** Finely ground quartzite rock.
- Plasticizer:** Material that increases the flexibility of a material.
- Plastisol:** Suspension of finely divided polymer in a liquid plasticizer with the plasticizer penetrating and plasticizing the polymer when heated.
- Promotor:** Coupling agent.
- Pultrusion:** Process in which bundles of resin-impregnated filaments are passed through an orifice and cured.
- Reinforced plastic:** Composite whose additional strength is dependent on a fibrous additive.
- Roving:** Bundle of untwisted strands.
- Side-chain crystallization:** Stiffening effect noted when long, regularly spaced pendent groups are present on a polymer chain.
- Sheet molding compound (SMC):** Resin-impregnated mat.
- Strand:** Bundle of filaments.
- Synergistic effect:** Enhanced effect beyond that expected by simply an additive effect.
- Syntactic foam:** Composite of resin and hollow spheres.
- Talc:** Naturally occurring hydrated magnesium silicate.
- Ultra-accelerator:** Catalyst that cures rubber at low temperatures.
- Ultraviolet stabilizer:** Additive that retards degradation caused by UV radiation.
- Vulcanization:** Cross-linking with heat and sulfur.
- Whiskers:** Single crystals used as reinforcement; extremely strong.
- Wood flour:** Attrition-ground, slightly fibrous wood particles.

EXERCISES

1. Name three unfilled polymers.
2. What is the continuous phase in wood?
3. What filler is used in Bakelite?

4. Name three laminated plastics.
5. How would you change a glass sphere from an extender to a reinforcing filler?
6. If one stirs a 5 mL volume of glass beads in 1 L of glycerol, which will have the higher viscosity, small or large beads?
7. When used in equal volume, which will have the higher viscosity: (a) a suspension of loosely packed spheres or (b) a suspension of tightly packed spheres?
8. Why is the segmental mobility of a polymer reduced by the presence of a filler?
9. What effect does a filler have on the T_g ?
10. Which would yield the stronger composite: (a) peanut shell flour or (b) wood flour?
11. What is the advantage and disadvantage, if any, of α -cellulose over wood flour?
12. What filler is used in decorative laminates such as Formica table tops?
13. What are potential advantages of natural fillers?
14. What is the disadvantage of using chipped glass as a filler in comparison to glass spheres?
15. What is the advantage of using BMC and SMC overhand layup techniques such as those used to make some boat hulls?
16. Which would be stronger: (a) a chair made from PP or (b) one of equal weight made from cellular PP?
17. What advantage would a barium ferrite-filled PVC strip have over an iron magnet?
18. Providing that the volumes of the fibers are similar, which would give the stronger composite: fibers with (a) small or (b) large cross sections?
19. How would you make an abrasive foam from polyurethane?
20. Why is a good interfacial bond between the filler surface and the resin important?
21. Cellulose nitrate explodes when softened by heat. What would you add to permit processing at lower temperatures?
22. PVC was produced in the 1830s but not used until the 1930s. Why?
23. What was the source of "fog" on the inside of the windshield until the 1930s.
24. Can you propose a mechanism for antiplasticization?
25. What naturally occurring fiber is more resistant to microbiological attack than nylon?
26. The T_g decreases progressively as the size of the alkoxy group increases from methyl to decyl in polyalkyl methacrylates but then increases. Explain.
27. PP is now used in indoor/outdoor carpets. However, the first PP products deteriorated rapidly when subjected to sunlight because of the presence of tertiary hydrogen atoms present. Explain.
28. Which is more resistant to attack by microorganisms: (a) PVC or (b) plasticized PVC?
29. Lead stearate is an effective thermal stabilizer for PVC, yet its use in PVC pipe is not permitted. Why?
30. When PVC sheeting fails when exposed long times to sunlight, it goes through a series of color changes before becoming black. Explain.
31. What is the advantage of using epoxidized soybean oil as a stabilizer for PVC?
32. Why do PVC films deteriorate more rapidly when used outdoors in comparison to indoors?
33. Which of the following is more resistant to UV light: (a) PP, (b) PE, or (c) PVC?
34. Sometimes, molded plastic have opaque material called "bloom" on the surface. Explain.
35. Why is the presence of static charges on polymers surfaces not desired?
36. Was carbon black always used as a reinforcing filler for tires?
37. Problem: Why does a tire filled with oxygen lose pressure faster than a tire filled with nitrogen gas?

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Synthesis of Reactants and Intermediates for Polymers

15

Many of the reactants used for the production of polymers are standard organic chemicals. However, because of the high purity requirements and large amounts needed, special conditions have been developed that allow large amounts of high purity reactants to be made in high yield. The first section of this chapter deals with the availability of the general feedstocks. The remaining sections deal with the synthesis of particular polymer reactants.

There is an industrial turn toward green materials. Much of this is found in developing processes that allow the creation of monomers from natural resources. You will see the move toward the creation of synthetic polymers from natural materials as you view Sections 15.2 and 15.3. The emphasis on green chemistry is also found when reactions produce “environmentally friendly” by-products or no by-products.

15.1 MONOMER SYNTHESIS FROM BASIC FEEDSTOCKS

Most of the monomers widely employed for both vinyl and condensation polymers are derived indirectly from simple feedstock molecules. This synthesis of monomers is a lesson in inventiveness. The application of the saying that “necessity is the mother of invention” has led to the sequence of chemical reactions where little is wasted and by-products from one reaction are employed as integral materials in another. Following is a brief look at some of these pathways traced from basic feedstock materials. It must be remembered that often many years of effort were involved in discovering the conditions of pressure, temperature, catalysts, etc., which must be present as one goes from the starting materials to the products.

“Fossil fuels” refer to materials formed from the decomposition of once living matter. Because these once living materials contain sulfur and heavy metals such as iron and cobalt, they must be removed either prior or subsequent to use.

The major fossil fuels are coal and petroleum. Marine organisms were typically deposited in muds and under water, where anaerobic decay occurred. The major decomposition products are hydrocarbons, carbon dioxide, water, and ammonium. These deposits form much of the basis for our petroleum resources. Many of these deposits are situated so that the evaporation of the more volatile products such as water and ammonia occurred, giving petroleum resources with little nitrogen- or oxygen-containing products. By comparison, coal is formed from plant material that has decayed to graphite carbon and methane.

Only about 5% of the fossil fuels consumed today are used as feedstocks for the production of today’s synthetic carbon-based products. This includes the products produced by the chemical and drug industries with a major portion acting as the feedstocks for plastics, elastomers, coatings, fibers, etc.

The major petroleum resources contain linear, saturated hydrocarbons (alkanes), cyclic alkanes, and aromatics. For the most part, this material is considered to have low free energy content.

An oil or petroleum refinery plant is the location where crude oil is processed and refined into groups of compounds with similar boiling points by a process called fractionation (Picture 15.1). Table 15.1 contains a brief listing of typical fraction-separated materials. Accompanying or subsequent to this fractionation occurs a process called “cracking,” whereby the hydrocarbon molecules are heated over catalysts that allow the hydrocarbon molecules to break up and then



PICTURE 15.1 Refinery plant in Louisiana.

TABLE 15.1 Typical Straight Chain Hydrocarbon Fractions Obtained from Distillation of Petroleum Resources

Boiling Range (°C)	Average Number of Carbon Atoms	Name	Uses
<30	1–4	Gas	Heating
30–180	5–10	Gasoline	Automotive fuel
180–230	11,12	Kerosene	Jet fuel, heating
230–300	13–17	Light gas oil	Diesel fuel, heating
300–400	18–25	Heavy gas oil	Heating

reform into structures that contain more branching that allow for appropriate combustion in our automobiles and trucks. Under other conditions, the cracking allows the formation of other desired feedstock molecules including methane, ethane, ethylene, propylene, and benzene that eventually become our plastics, fibers, elastomers, sealants, coatings, composites, etc.

What is not always appreciated is the similarity of the feedstocks for petroleum products mainly employed for transportation and those used by the polymer and other chemical industries. But there is a divergence of catalytic treatments used to derive each of these groups of materials. As already noted, petroleum is generally derived from the decomposition of plant and less so animal life. Much of this material is saturated linear hydrocarbons mainly coming from the linear cell walls and related materials. The term “**cracking**” is used to describe much of the conversion of raw petroleum to the end products. The term cracking is an apt term since the linear, or even branched, materials are broken, cracked, and allowed to reform under specific conditions employing specific conditions. In the case of fuel, the saturated hydrocarbons are the desired products, while for most of the chemical conversions necessary for the production of monomers, drugs, etc., unsaturated feedstocks are necessary that allow the exploitation of the unsaturation to synthesize needed products.

In catalytic cracking, the petroleum materials are broken and directed through the use of specific catalysts and reaction conditions forming a variety of branched saturated products. These saturated hydrocarbons are less reactive than unsaturated materials. In steam cracking, the petroleum materials are broken apart under conditions that encourage formation of unsaturation, generally the formation of alkenes.

There is a third form of cracking that is less used today in the production of feedstocks from petroleum but it was a forerunner for the other two cracking processes. “**Thermal cracking**” was the initial form of cracking employed. In 1855, Benjamin Silliman of Yale described the formation of decomposition products from the distillation of rock oil that might be of economic use. Rock oil was indeed petroleum with the term petroleum derived from the Latin *petra* (rock) and *oleum* (oil). The formation of coke, a hard porous industrial waste consisting of largely carbon, was a problem in thermal cracking. Every several days, the still had to be shut down to allow the removal of the coke. Thermal cracking gave way to steam cracking.

During the 1920s, Union Carbide and Standard Oil of New Jersey developed strategies to convert petroleum to ethylene and propylene through steam cracking. Standard Oil, in 1920, produced the initial petrochemical, isopropanol. Isopropanol was the result of the reaction of propylene and water in the presence of acid. While we know isopropanol as rubbing alcohol, it was originally oxidized to acetone a solvent used as a component for preparing the explosive Cordite used in World War I. Cordite is a family of smokeless propellants used to manufacture bullets and other projectiles and it is related to dynamite so it is historically important and helped create the wealth behind Nobel.

Supposedly, the first catalytic cracking agent was discovered by A. J. Houdry in the 1920s when he was searching for a way to make better gasoline for his race car. His “magic” catalyst was found in nearby clays and was, in fact, zeolites. The zeolites are natural products that contain highly charged channels that allow petroleum materials to pass through them with some structural constraints. These natural zeolites allowed the breakup and reformation of the petroleum into more branched hydrocarbons. These branched hydrocarbons burned slower than the linear hydrocarbons allowing an engine to capture more of the energy formed thus increasing the efficiency of the engine. The natural catalysts had problems and the pores were easily clogged with our old nemesis coke. Heat was used to drive off the coke and this heat damaged the catalysts. (Today, synthetic zeolites are employed.) Even so, two companies were established using this technology—Sun Oil Company and Socony Vacuum Oil Company now ExxonMobil Oil Company. Plants were built in 1936 and, along with Phillips Petroleum Company, supplied fuel critical for our armed services for World War II.

Standard Oil Development Company worked with W. K. Lewis of MIT to produce powered zeolite catalysts. This evolved into a process called fluidized catalytic cracking where the powered catalyst is fluidized. These stories and the topic of cracking are described in greater detail by Mark Green and Harold Wittcoff (2003) in *Organic Chemistry: Principles and Industrial Practice*, Wiley-VCH.

In 1925, Phillips Petroleum Company was only one of dozens of small oil companies in Oklahoma. The only distinction was the large amount of natural gasoline (or naphtha), the lightest liquid fraction (Table 15.1), found in its crude oil. As was customary, Phillips, and most of the other oil companies of the time, employed a distillation process to isolate the butane and propane. Even so, they were sued by larger companies for the use of this distillation process probably because they were small, had no real research capacity of their own, and no real legal defense team. Frank Phillips elected to fight supposedly including an argument that the ancient Egyptians had used a similar process to create an alcoholic equivalent to an Egyptian alcoholic drink. Phillips won the suit but became convinced that if the company was to remain successful, it would need to have a research effort.

During the early dust bowl years, 1935, they established the oil industry’s first research team in Bartlesville, OK. George Oberfell, hired by Phillips to fight the lawsuit, planned the initial research efforts that involved three main initiatives. First, develop technology to use light hydrocarbons in new ways as motor fuels. Second, develop markets for butane and propane. And finally, find new uses for the light hydrocarbons outside the fuel market. All three objectives were achieved.

Frederick Frey and Walter Schultze were instrumental early researchers. Frey was among the first to dehydrogenate paraffins catalytically to olefins and then the olefins to diolefins that serve as feedstocks to the production of many of today’s polymers. In competition with Bakelite, he discovered the preparation of polysulfone polymers made from the reaction of

sulfur dioxide and olefins creating a hard Bakelite-like material. Frey and Schultze also developed a process that allowed the production of 1,3-butadiene from butane that allowed the synthesis of synthetic rubber.

Probably, Frey's most important invention involved the use of hydrogen fluoride to convert light olefins, produced as by-products of a catalytic cracker, into high octane motor and aviation fuels. This process is still widely used. It came at a critical time for America's World War II efforts allowing fuel production for the allied forces. This fuel allowed aircraft faster liftoffs, more power, and higher efficiency.

As noted before, there is a major difference between steam and catalytic cracking. In steam cracking, free radicals are formed while in catalytic cracking, carbocations are formed.

Steam cracking generally is a gas phase reaction that occurs in the absence of a polar solvent or catalysis. In the absence of polar solvent or catalyst, chemical bonds exposed to sufficient energy will break homolytically producing free radicals. Carbon-carbon bonds are fairly strong being on the order of 350 kJ/mole. Even at the relatively high temperatures employed for steam cracking, 600°C–900°C for only milliseconds, there is not sufficient energy for the extent of cracking observed. But small amounts of free radicals are formed that allow a chain reaction to occur, just as in the case of the free radical reactions forming vinyl polymers. In effect, the steam cracking conditions allow the initiation reaction to occur leading to the production of various unsaturated products employed by the chemical industry. As in the case with the free radical polymerization, the activation energy for propagation is small. Unlike free radical polymerization where the concentration of vinyl-containing monomers is large, here the concentration of saturated hydrocarbons is large so reaction of a free radical with another saturated hydrocarbon is large creating an ongoing, chain process where one free radical creates many chain scissions rather than polymers. In the propagation step, beta-scissions occur leaving a site of unsaturation and creation of a hydrogen free radical that continues the process. Figure 15.1 contains the major steps that occur in the steam cracking process. Notice the similarity to the typical free radical kinetic sequence.

By comparison, carbocations are formed in the employed *catalytic cracking* processes. Initially, the mechanism of catalytic cracking was not understood. Soon, it was discovered that the presence of a Bronsted acid was needed for the reaction to occur in the zeolites. It was also discovered that isomerizations were common giving branched products. The products are formed by the intervention of carbocations. These carbocations are formed from the petroleum molecules or their thermally cracked products through reaction with the acidic sites in the zeolites. The carbocations undergo rearrangements that interconvert constitutional isomeric forms.

While the stabilities between the active forms for both carbocations and free radicals are similar, the energy difference for structural change in free radicals is much smaller than for

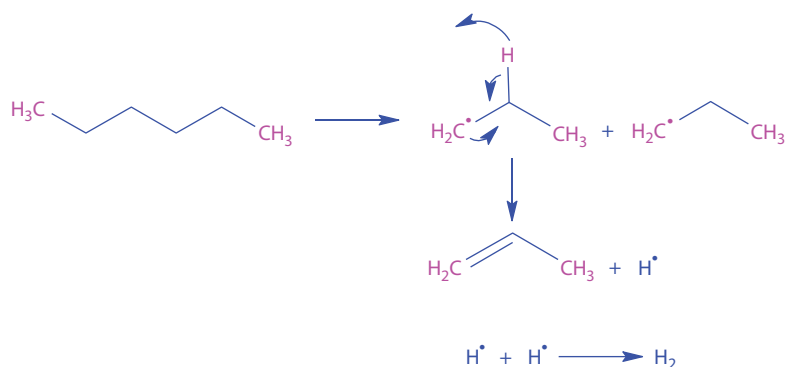


FIGURE 15.1 General reaction scheme for the steam catalytic reaction with hexane. The top reaction describes one of the initiation steps, second arrow describes one of the propagation steps, and the last line describes one of the termination steps.

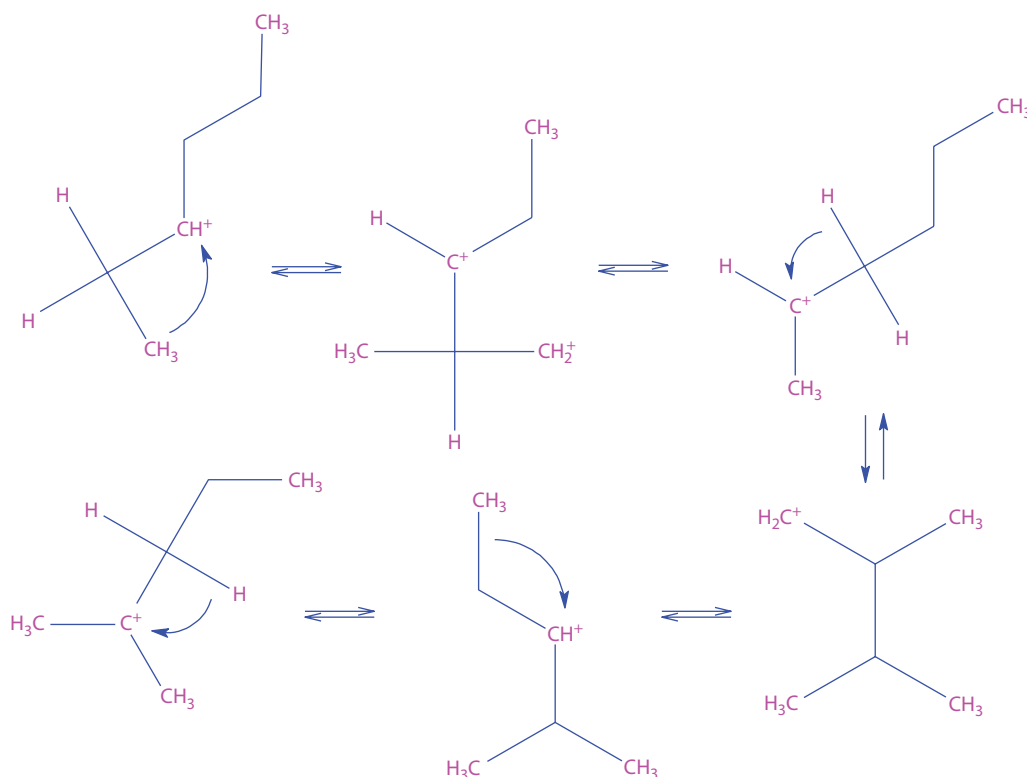


FIGURE 15.2 Illustration of rearrangements that occur through movement of carbocation reactive site for linear hexane.

carbocations. The chief driving force for rearrangement in carbocations is the formation of structurally more stable branched compounds (Figure 15.2). Tertiary carbocations are more stable than secondary carbocations, which in turn are more stable than primary carbocations, thus the tendency to form branches that allow more stable carbocations. For hexane in the steam catalytic reaction, beta-scission forming carbocations would produce primary carbocations, not a favored stable carbocation. Thus, the stability of tertiary and secondary carbocations favors branching but not beta-bond scission.

Next, why is there no tendency for branching in the free radical steam cracking? Molecular orbital formulations prohibit 1,2-rearrangements of free radicals so that carbon migration is prohibited. Again, the textbook, by Mark Green and Harold Wittcoff (2003), *Organic Chemistry: Principles and Industrial Practice*, Wiley-VCH, contains an expanded version of this.

The major one carbon feedstock is methane and it serves as the feedstock to a number of important monomers including hexamethylene tetramine and melamine, used in the synthesis of a number of cross-linked thermosets as well as vinyl acetate, ethylene, ethylene glycol, and methyl methacrylate (Figure 15.3). Today, methane is becoming increasingly important due to the discovery of vast storehouses of methane both through shell fracking and natural gas fields.

Formaldehyde, produced in the methane stream, serves as the basis for the formaldehyde-intensive resins, namely, phenol-formaldehyde, urea-formaldehyde (UF), and melamine-formaldehyde resins, as noted earlier. Formaldehyde is also involved in the synthesis of ethylene glycol, one of the two comonomers used in the production of PET. Formaldehyde also serves as the basic feedstock for the synthesis of polyacetals.

Another important use for methane is its conversion to synthesis gas (or syngas), a mixture of hydrogen gas and carbon monoxide as shown in Figure 15.3. Synthesis gas can also be derived from coal. When this occurs, it is called water gas. Interestingly, the reaction of methane giving

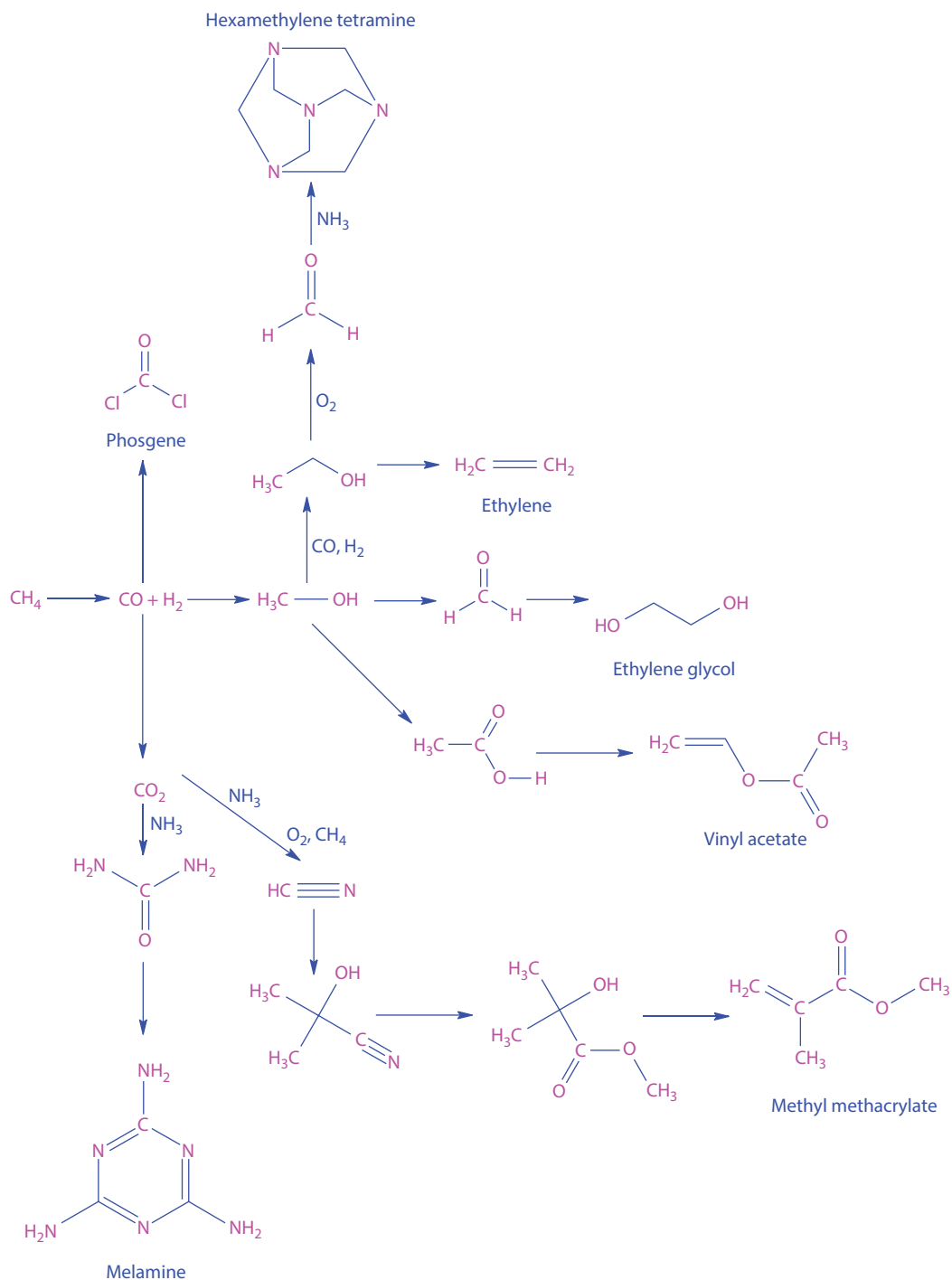


FIGURE 15.3 Monomer synthesis chemical flow diagram based on methane feedstock.

carbon monoxide and hydrogen can be reversed so that methane can be produced from coal through this route.

One major two-carbon feedstock is ethylene. From Figure 15.4, you can see that a number of the monomers are directly synthesized from ethylene. Again, while the “react” arrow goes directly from ethylene to the product, as noted earlier, it often took years to develop an economical procedure to obtain the product in essentially 100% yield. Here, depending on the reaction conditions, a wide variety of intermediates and products are formed that allow the synthesis of

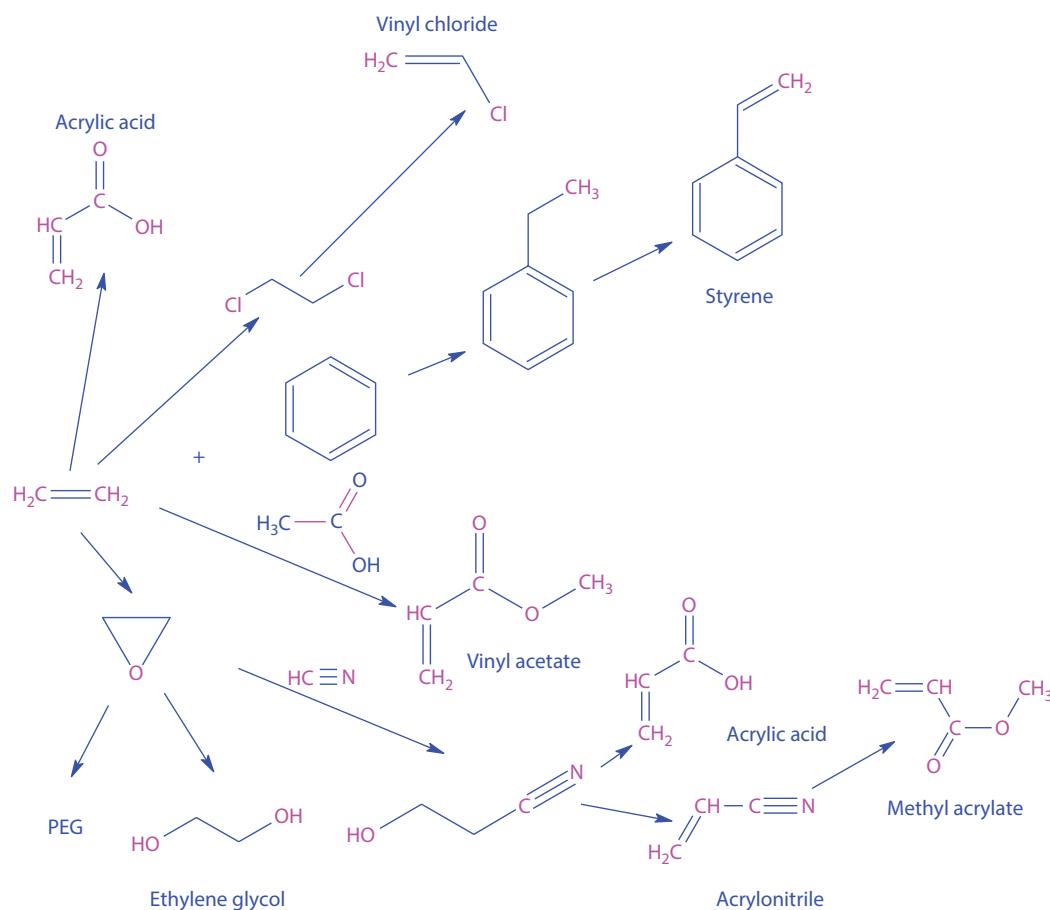


FIGURE 15.4 Monomer synthesis chemical flow diagram based on ethylene feedstock.

a number of polymers including poly(acrylic acid), poly(vinyl chloride), polystyrene, poly(vinyl acetate), polyesters (in particular PET), and poly(methyl acrylate). Of course, ethylene is itself part of the polymer feedstock pool being the feedstock for all of the polyethylenes.

One of the special recent emphases is the creation of feedstock material that has not come from petroleum but now from natural, renewable feedstock materials. This theme has been described throughout this text and with each new edition, more examples will be present. The production of ethanol from biomass employing bacterium has been known for over a decade but now is becoming more efficient. Thus, the use of particular tailored bacterium now allows the biosynthesis of ethanol in over 70% yield. As shown in Figure 15.3, ethanol is a gateway to the formation of ethylene and from ethanol other monomers as shown in Figure 15.4.

Another two-carbon feedstock is acetylene. Acetylene is typically obtained from coal by converting coke calcium carbide and then treating the calcium carbide with water. As shown in Figure 15.5, a number of important monomers can be made from acetylene. Even so, because of the abundance of other feedstocks from petroleum reserves, only some of the routes shown in Figure 15.5 are widely used.

Propylene is the basic three-carbon building block (Figure 15.6). Again, its polymerization gives polypropylene. The ingeniousness of some of the synthetic routes is shown in the conversion of benzene, through reaction with propylene, to cumene and the consequent oxidation forming phenol and acetone that is subsequently converted to bisphenol A, a basic building block for certain polyesters. Phenol is involved in the synthesis of the phenol-formaldehyde resins, adipic acid, and 1,6-hexamethylenediamine. Acetone, in turn, is also involved in numerous important synthetic steps either as a reactant or solvent. It is involved in the synthesis of methyl methacrylate and isoprene.

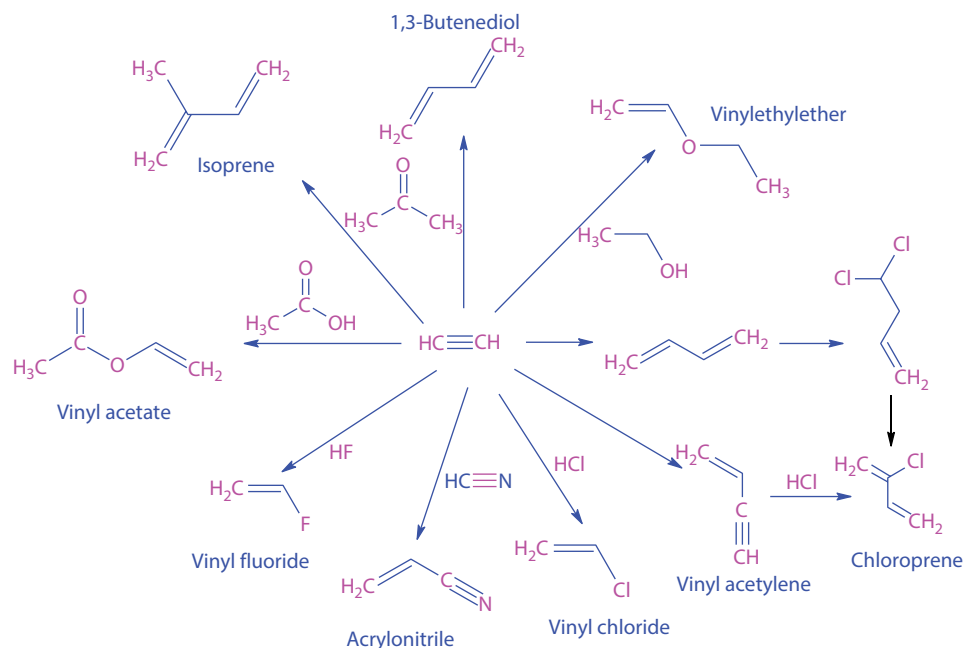


FIGURE 15.5 Monomer synthesis chemical flow diagram based on acetylene feedstock.

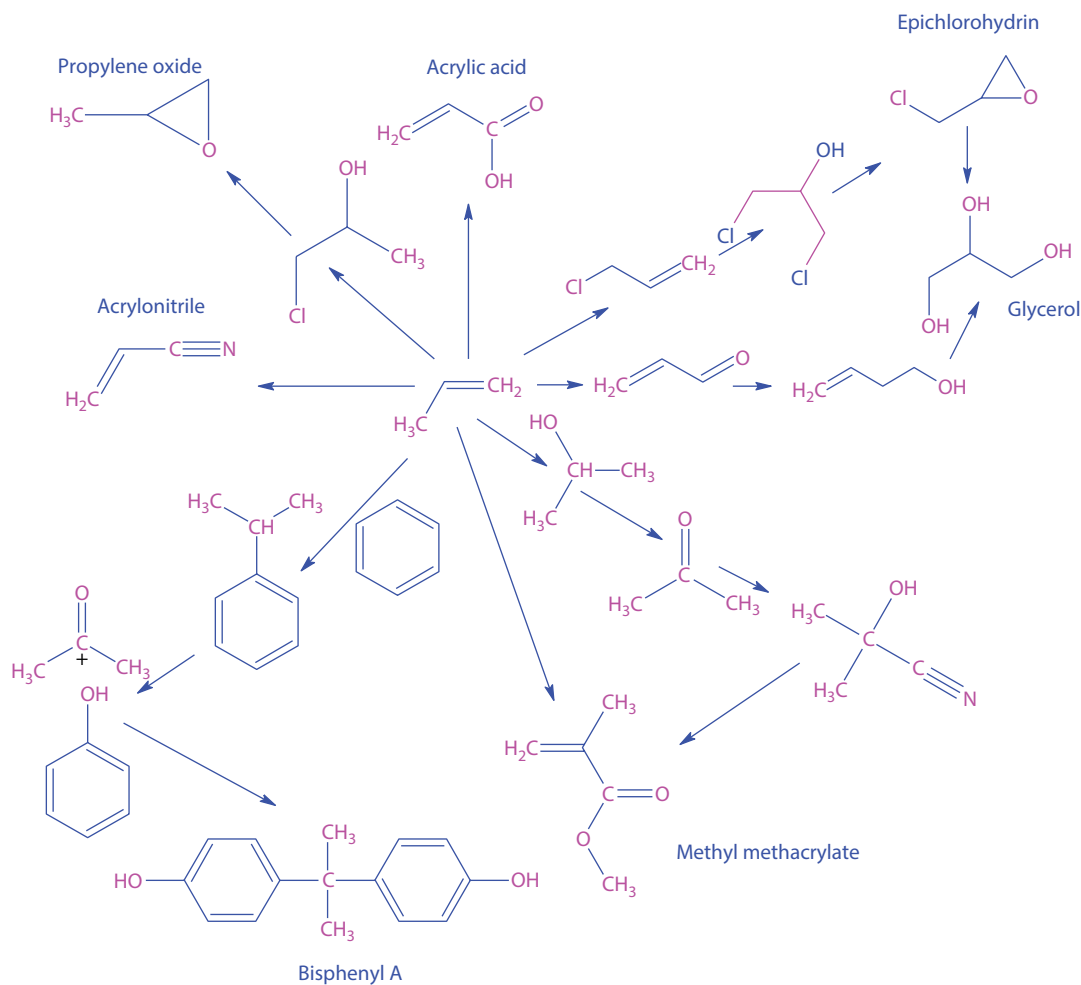


FIGURE 15.6 Monomer synthesis chemical flow diagram based on propylene feedstock.

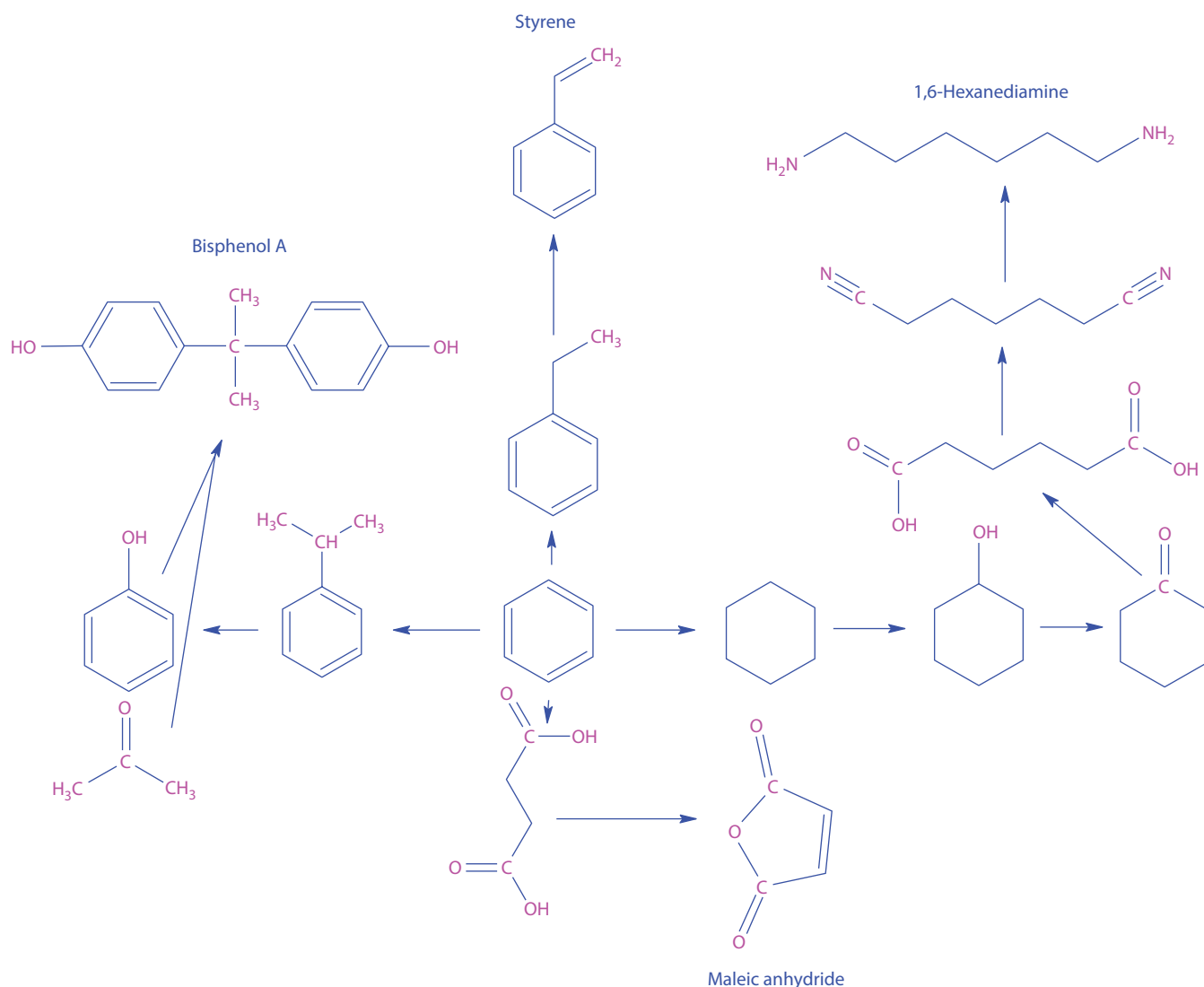


FIGURE 15.7 Monomer synthesis chemical flow diagram based on benzene feedstock.

The major four-carbon feedstock molecules are 1,3-butadiene and isobutylene, both involved in the synthesis of many monomers and intermediates. Butadiene is copolymerized with styrene to form SBR rubber and with acrylonitrile to form ABS rubbers.

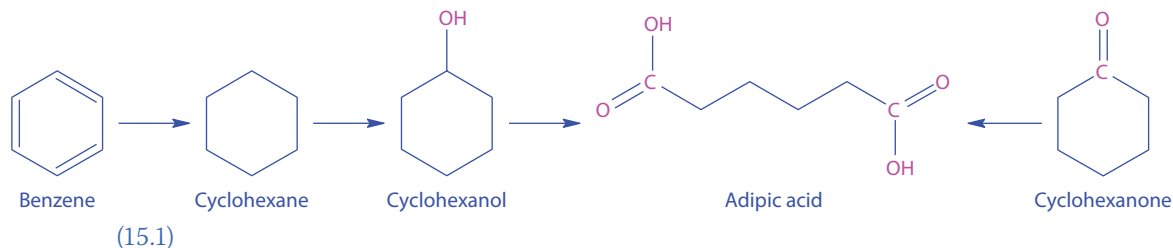
Benzene forms the basis for a number of monomers (Figure 15.7) including those that retain their aromatic character like styrene and those that do not, like adipic acid.

In summary, monomer synthesis from basic, readily available inexpensive feedstocks based on fossil fuels is both an art and a science developed over the past half century or so. It represents a delicate balance and interrelationship between feedstocks and the so-called by-products from one reaction that are critical reactants in another reaction. Monomer and polymer synthesis continues to undergo change and improvement as the natural environment and societal and worker health continue to be dominant factors. Many of these and other monomers are now being produced by various microbes. Some of these efforts are described here and in Sections 16.15 and 16.16.

15.2 REACTANTS FOR STEP-REACTION POLYMERIZATION

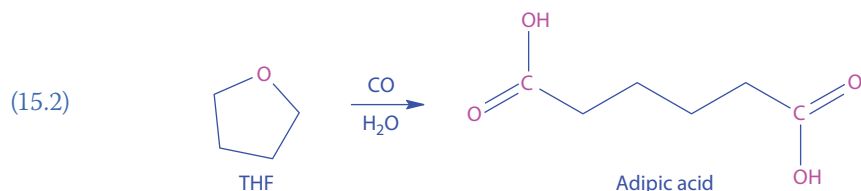
Adipic acid (1,4-butanedicarboxylic acid) is used for the production of nylon 66 and may be produced from the oxidation of cyclohexane (Equation 15.1). Cyclohexane is obtained by the Raney

nickel-catalytic hydrogenation of benzene. Both the cyclohexanol and cyclohexanone are oxidized to adipic acid by heating with nitric acid.

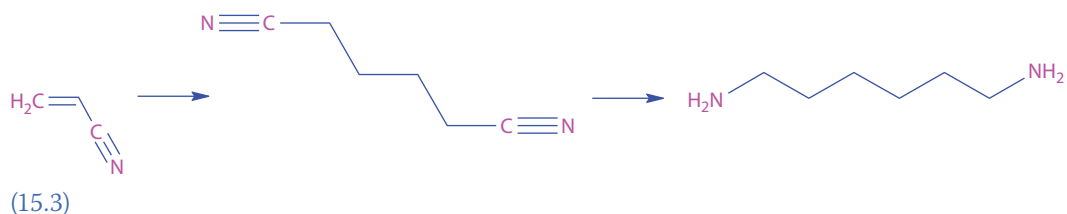


A new method that emphasizes green chemistry principles involves oxidizing cyclohexene with hydrogen peroxide through a tungsten catalyst and a phase transfer catalyst producing adipic acid and water as the by-product.

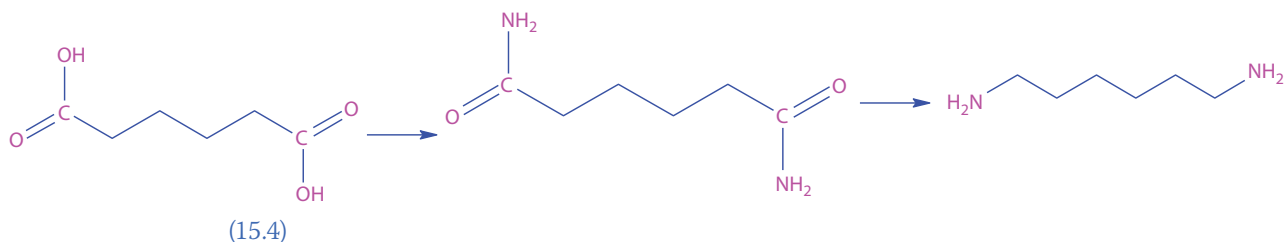
Adipic acid can also be made from tetrahydrofuran (THF), obtained from furfural a naturally derived material (Equation 15.2). It is carbonylated in the presence of nickel carbonyl–nickel iodide catalyst. Furfural is a chemurgic product obtained by the steam-acid digestion of corn cobs, oat hulls, bagasse, or rice hulls.



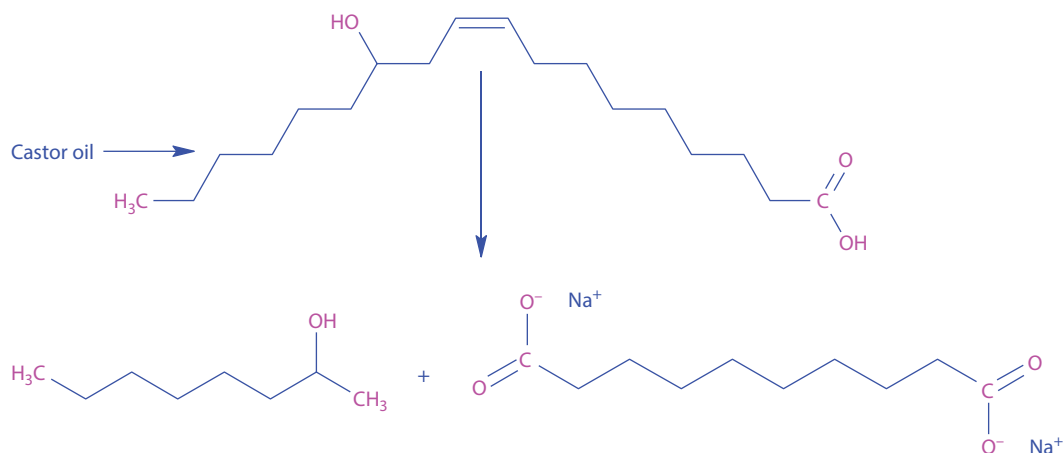
Adiponitrile may be produced from the hydrodimerization of acrylonitrile or from 1,3-butadiene via 1,4-dicyanobutene-2. Adiponitrile is then hydrogenated forming 1,6-hexanediamine (Equation 15.3).



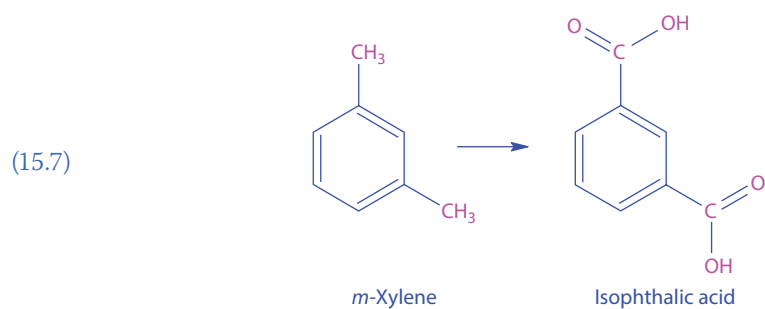
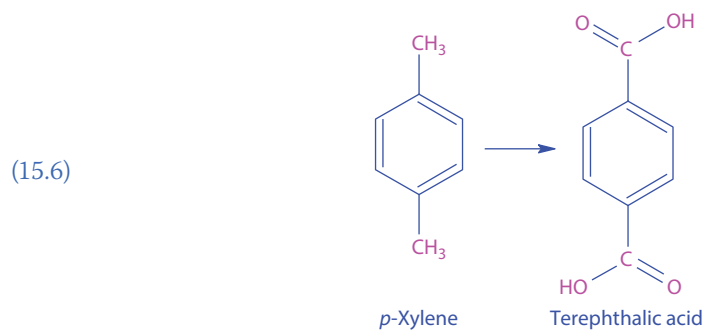
1,6-Hexanediamine can also be made by the liquid phase catalytic hydrogenation of adiponitrile or adipamide, which is made from adipic acid (Equation 15.4).



Sebacic acid (1,8-octane dicarboxylic acid), which is used to make nylon-610, has been produced from 1,3-butadiene and by the dry distillation of castor oil (ricinolein). The cleavage of ricinoleic acid gives 2-octanol and the salt of sebacic acid (Equation 15.5).

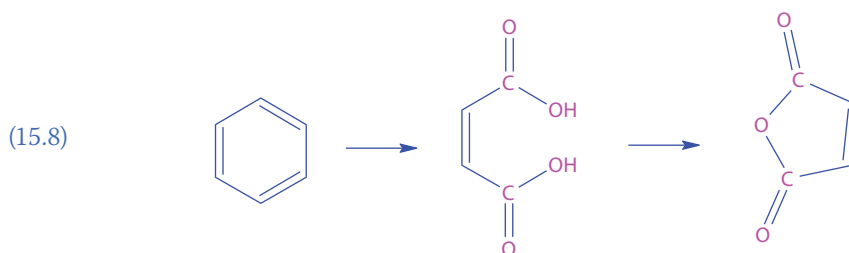


Phthalic acid (1,2-benzene dicarboxylic acid), terephthalic acid (1,4-benzene dicarboxylic acid; Equation 15.6), and isophthalic acid (1,3-benzene dicarboxylic acid; Equation 15.7) are made by the selective oxidation of the corresponding xylenes. The oxidation of *p*-xylene by oxygen from the air is generally done using acetic acid as a solvent in the presence of a catalyst such as cobalt–manganese. The yield is close to 100%.

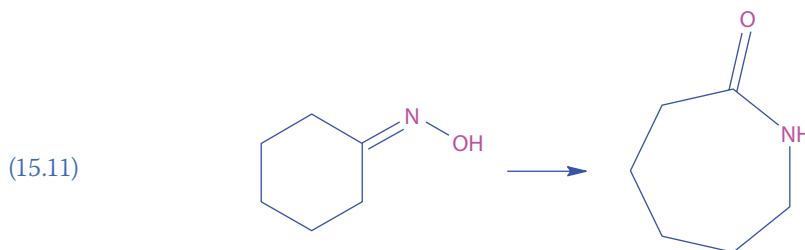
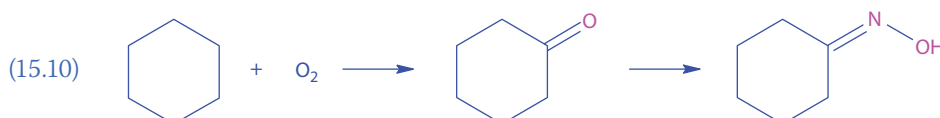


Terephthalic acid may also be produced from the oxidation of naphthalene and by the hydrolysis of terephthalonitrile.

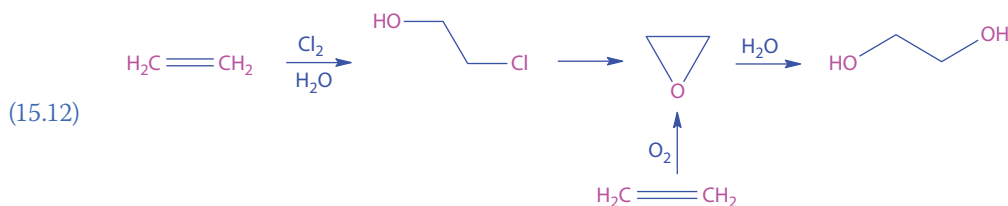
Maleic anhydride (2,5-furandione) is made as a by-product in the production of phthalic anhydride and by the vapor phase oxidation of butylene or crotonaldehyde. It is also obtained by the dehydration of maleic acid and by the oxidation of benzene (Equation 15.8). Maleic anhydride is used for the production of unsaturated polyester resin. This reactant, like many reactants, is fairly toxic and should be treated as such.



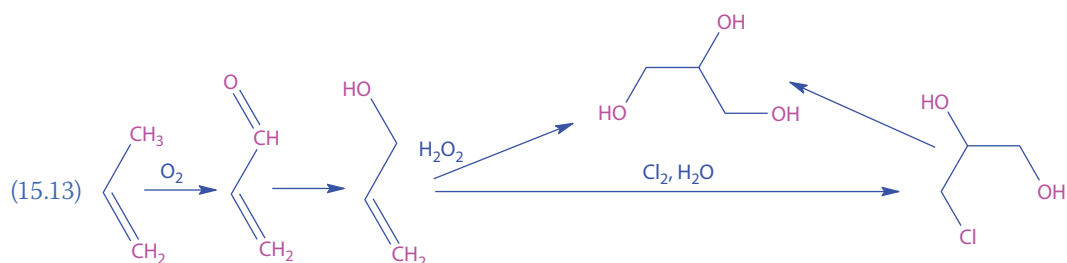
2-Pyrrolidone is a lactone used for the production of nylon-4. This reactant may be produced by the reduction ammoniation of maleic anhydride. ϵ -Caprolactam, used in the production of nylon 6, may be produced using several approaches. The oxime may be produced by the catalytic hydrogenation of nitrobenzene, the photolytic nitrosylation of cyclohexane (Equation 15.9), or the reaction of cyclohexanone and hydroxylamine (Equation 15.10) or by the Beckman rearrangement of cyclohexanone oxime (Equation 15.11). Nearly one-half of the production of caprolactam is derived from phenol.



Ethylene oxide, used for the production of ethylene glycol and poly(ethylene oxide), is obtained by the catalytic oxidation of ethylene (Equation 15.12). Ethylene glycol, used in the production of PET, is produced by the hydrolysis of ethylene oxide.

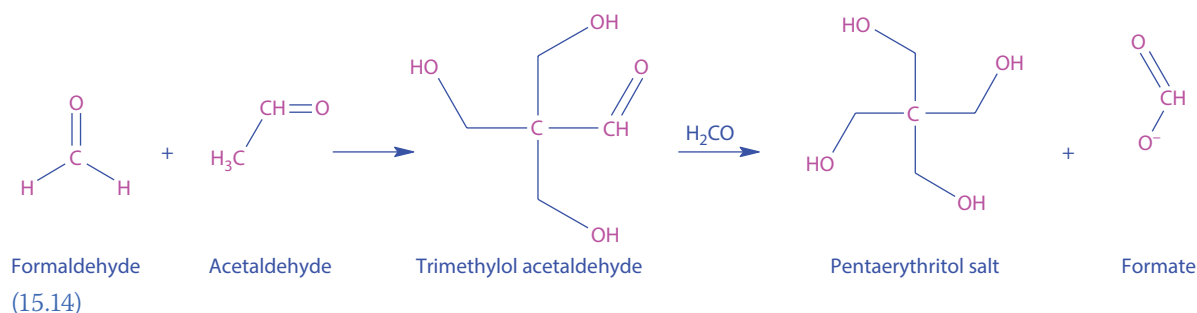


Glycerol, used for the production of alkyds, is produced by the catalytic hydroxylation or the hypochlorination of allyl alcohol. Allyl alcohol is produced by the reduction of acrolein, which is, in turn, obtained by the oxidation of propylene (Equation 15.13).

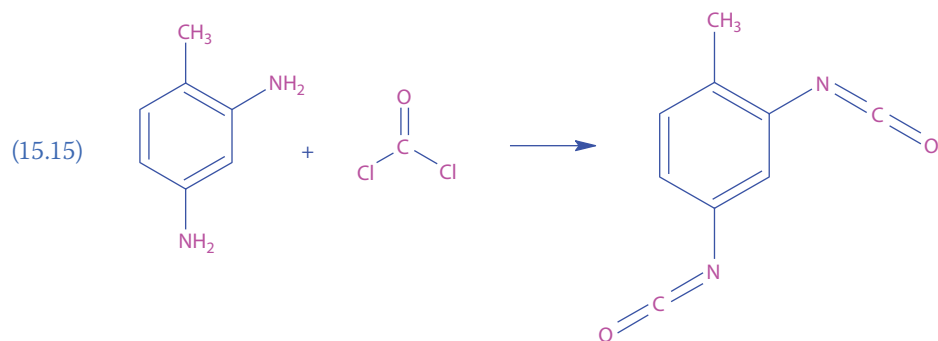


Until recently, glycerol was obtained mainly from epichlorohydrin. But because glycerol forms the backbone of fats, it is produced as the fats are degraded giving the fatty acid and glycerol. It is also a by-product of the production of biodiesel production through the transesterification of vegetable oils. Thus, glycerol is almost solely obtained today from these “natural” sources.

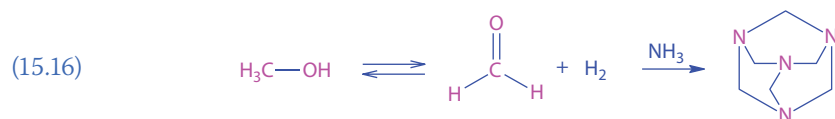
Pentaerythritol, used in the production of alkyds, is produced by a crossed Cannizzaro reaction of the aldol condensation product of formaldehyde and acetaldehyde (Equation 15.14). The by-product formate salt is a major source of formic acid.



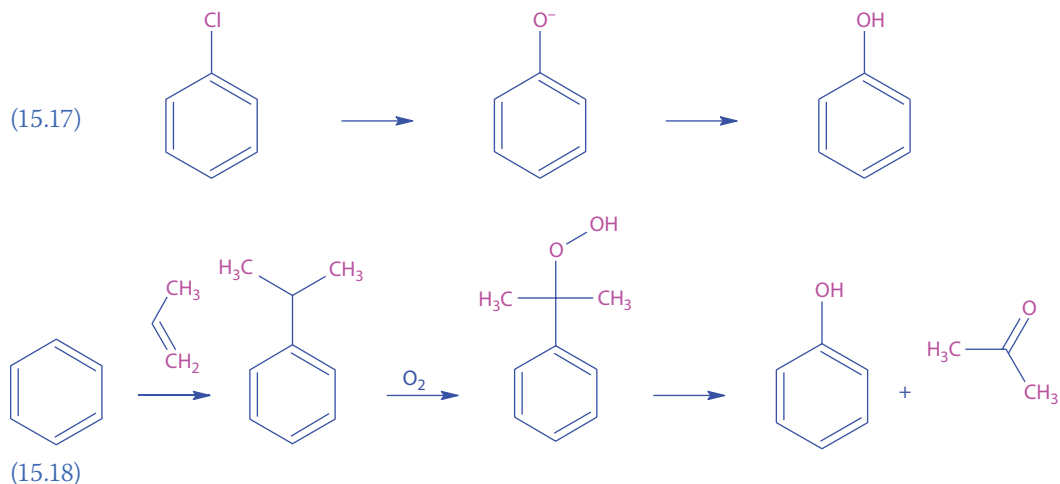
2,4-Toluene diisocyanate (TDI), used for the production of polyurethanes and polyureas, is obtained by the phosgenation of 2,4-toluenediamine (Equation 15.15). Phosgene is obtained by the reaction of chlorine and carbon monoxide.



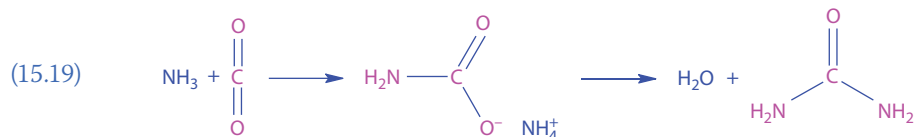
Formaldehyde is employed as a basic unit for many industrial adhesives such as the phenolic plastics formed from the reaction of phenol and formaldehyde. It also serves as one of the reactants in the formation of amino plastics in the production of UF resins. Formaldehyde can self-condense forming the cyclic trimer trioxane and the polymer paraformaldehyde. It is industrially produced from the catalytic oxidation of methanol. In turn, hexamethylenetetramine is produced by the condensation of ammonia and 30% aqueous formaldehyde (formalin; Equation 15.16).



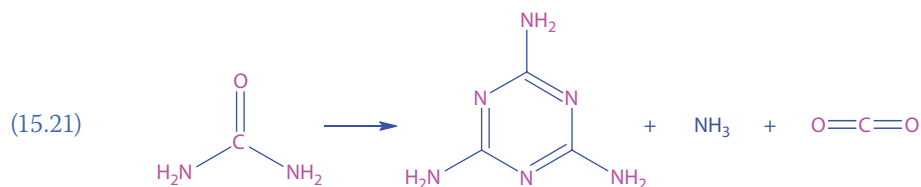
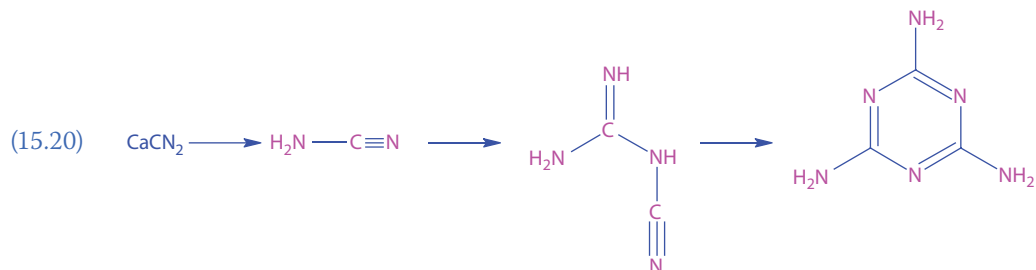
While some phenol is produced by the nucleophilic substitution of chlorine in chlorobenzene by the hydroxyl group (Equation 15.17), most is produced by the acidic decomposition of cumene hydroperoxide (Equation 15.18) that also gives acetone along with the phenol. Some of the new processes for synthesizing phenol are the dehydrogenation of cyclohexanol, the decarboxylation of benzoic acid, and the hydrogen peroxide hydroxylation of benzene.



Urea is highly water soluble and offers an efficient avenue for the human body to expel excess nitrogen. The individual atoms come from water, carbon dioxide, aspartate, and ammonia and are involved in the urea cycle metabolic pathway. Urea, which is used for the production of UF resins, is made by the *in situ* decomposition of ammonium carbamate, which is made by the condensation of ammonia and carbon dioxide at 200°C and 200 atm (Equation 15.19).

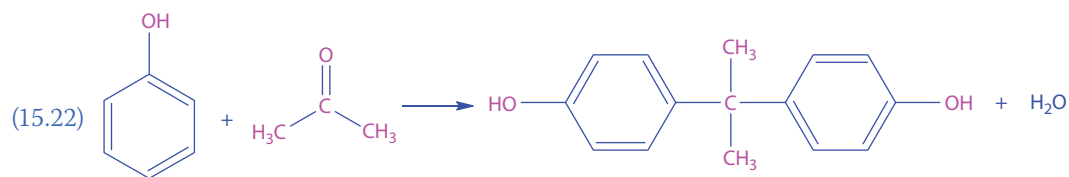


Melamine (cyanuramide), used in the production of melamine-formaldehyde resins, is obtained by heating dicyanodiamide (Equation 15.20), which is obtained by heating cyanamide. Today, most melamine is produced by heating urea (Equation 15.21)

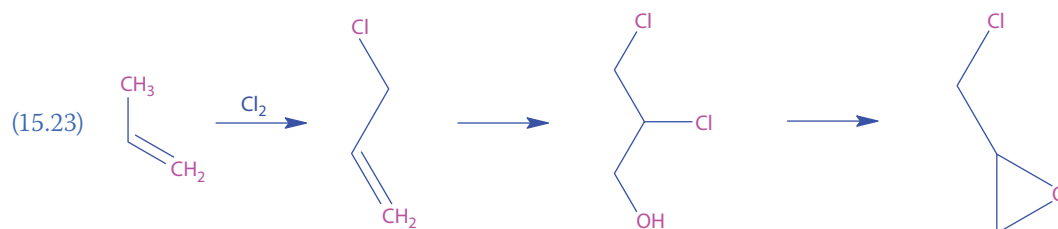


Bisphenol A [(bis-4-hydroxyphenol)dimethylmethane], used for the production of epoxy resins and polycarbonates, is obtained by the acidic condensation of phenol and acetone (Equation 15.22).

Here, the carbonium ion produced by the protonation of acetone attacks the phenol molecule at the para position producing a quinoidal oxonium ion that loses water and rearranges to a *p*-isopropylphenol carbonium ion. The water attacks another phenol molecule, also in the para position, giving another quinoidal structure that rearranges to bisphenol A. It has been found that bisphenol A may be involved in one of the endocrine systems. The consequences of this are still being determined.



Epichlorohydrin (chloropropylene oxide) is used for the production of epoxy resins. It is produced by the dehydrochlorination of 2,3-dichloro-1-propanol (Equation 15.23). The hydrin is produced by the chlorohydration of allyl chloride.

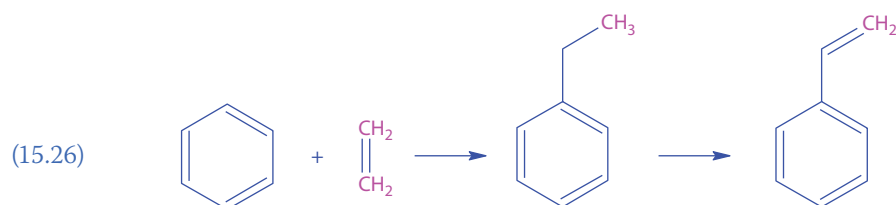


Methyltrichlorosilane is produced by the Grignard reaction of silicon tetrachloride and methylmagnesium chloride (Equation 15.24). Dimethyldichlorosilane, used in the synthesis of polydimethylsiloxane, is obtained by the reaction of methylmagnesium chloride and methyltrichlorosilane (Equation 15.25).

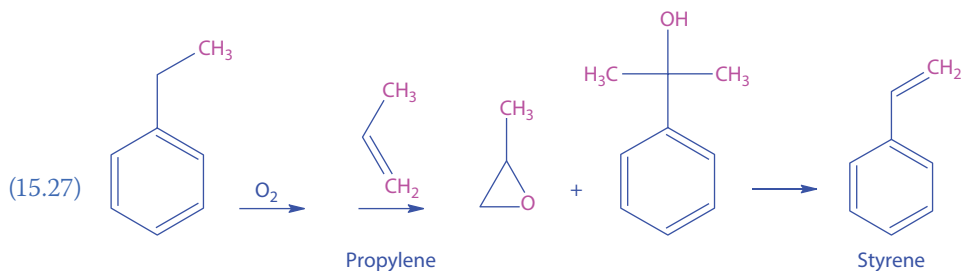


15.3 SYNTHESIS OF VINYL MONOMERS

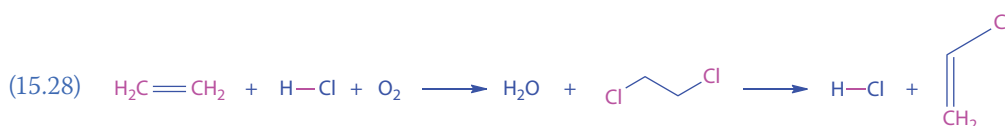
Styrene is generally produced by the catalytic vapor phase dehydrogenation of ethylbenzene (Equation 15.26). Ethylbenzene is made by the Friedel–Crafts condensation of ethylene and benzene. Ethylbenzene, in the vapor phase, is passed over a solid catalyst bed. Most catalysts are based on iron(III) oxide containing potassium oxide or potassium carbonate. Steam serves several roles acting as an energy source, and it removes coke that forms on the iron oxide catalyst. Typically, several reactors are used in series with each “pass” of the vapor ethylbenzene resulting in increased styrene production. The main by-products are benzene and toluene. Styrene is also produced by the palladium acetate-catalyzed condensation of ethylene and benzene and by the dehydration of methylphenylcarbinol obtained by the propylation of ethylbenzene. Because of the toxicity of styrene, its concentration in the atmosphere must be severely limited.



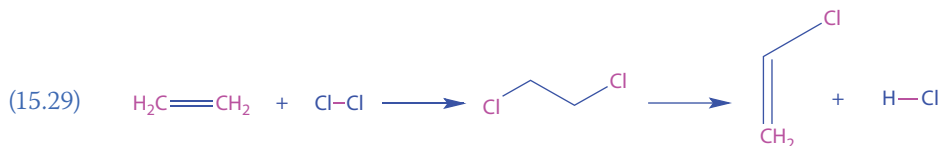
A process to produce styrene monomer and propylene oxide simultaneously was introduced in 1969, and it is also employed to produce styrene industrially (Equation 15.27).



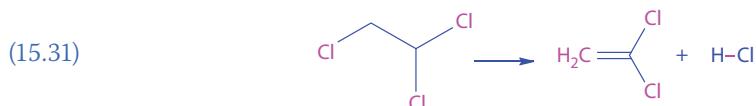
Vinyl chloride, formerly obtained from acetylene, is now produced by the transcatalytic process where chlorination of ethylene, oxychlorination of the by-product hydrogen chloride, and dehydrochlorination occur in a single reactor (Equation 15.28).



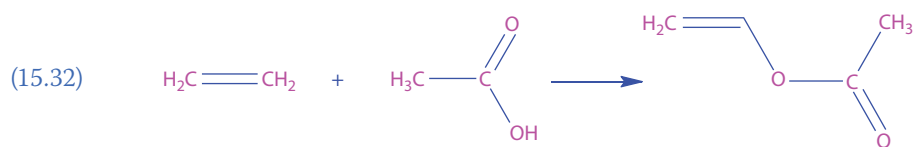
Vinyl chloride is also produced by the direct chlorination of ethylene and the reaction of acetylene and hydrogen chloride (Equation 15.29). The hydrogen chloride generated in the chlorination of ethylene can be employed in reaction with acetylene allowing a useful coupling of these two reactions (Equation 15.30). Today, most vinyl chloride is produced from reaction of ethylene and chlorine forming ethylene dichloride. The ethylene dichloride is heated under pressure resulting in its decomposition to vinyl chloride and hydrogen chloride (Equation 15.29).



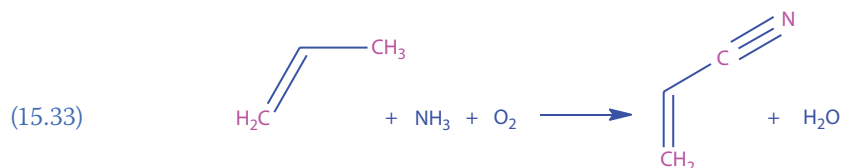
Vinylidene chloride, or 1,1-dichloroethene, is produced by the pyrolysis of 1,1,2-trichloroethane at 400°C in the presence of lime or base (Equation 15.31). Since both vinylidene chloride and vinyl chloride are carcinogenic, their concentrations must be kept low. It was widely used to form polymer, mainly poly(vinylidene chloride), which formed the basis for a cling wrap called Saran wrap. Research suggested that Saran wrap may pose a health danger by leaching when microwaved. Because of this, most cling wrap formulations have changed to polythene (polyethylene).



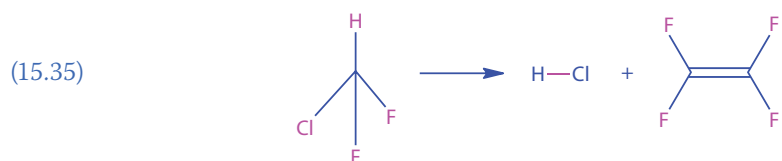
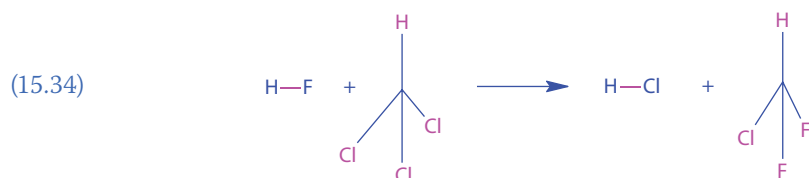
Vinyl acetate was produced by the catalytic acetylation of acetylene, but this monomer is now produced by the catalytic oxidative condensation of acetic acid and ethylene (Equation 15.32). Other vinyl esters can be produced by the transesterification of vinyl acetate with higher boiling carboxylic acids.



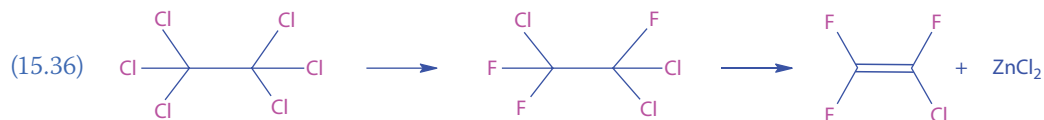
Acrylonitrile (vinyl cyanide) is produced by the Sohio process involving the ammoxidation of propylene (Equation 15.33). Again, since this monomer is carcinogenic, care must be taken to minimize exposure to it.



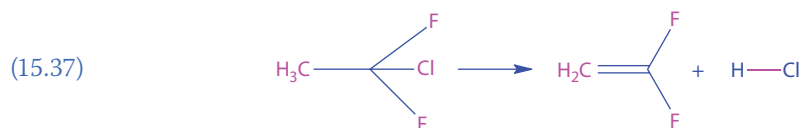
Tetrafluoroethylene is produced from the thermal dehydrochlorination of chlorodifluoromethane (Equation 15.35) which, in turn, is produced from chloroform and HF (Equation 15.34).



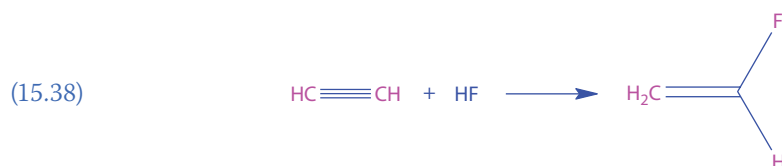
Trifluoromonoethene is obtained from the zinc metal dechlorination of trichlorotrifluoroethane (Equation 15.36). The latter is produced by the fluorination of hexachloroethane.



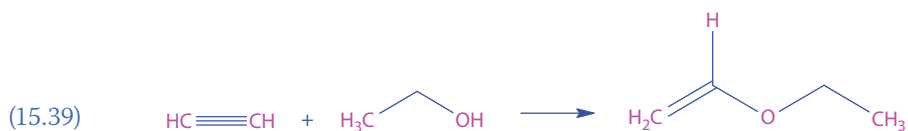
Vinylidene fluoride is produced by the thermal dehydrochlorination of 1-monochloro-1,1,-difluoroethane (Equation 15.37).



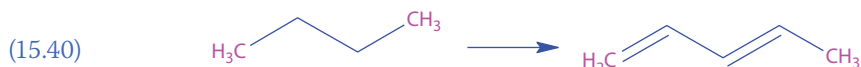
Vinyl fluoride may be obtained by the catalytic hydrofluorination of acetylene (Equation 15.38).



Vinyl ethyl ether is obtained by the ethanolysis of acetylene in the presence of potassium ethoxide (Equation 15.39).

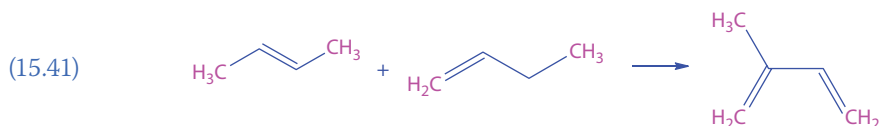


1,3-Butadiene, used for the production of elastomers, is produced by the catalytic thermal cracking of butane and as a by-product of other cracking reactions (Equation 15.40).

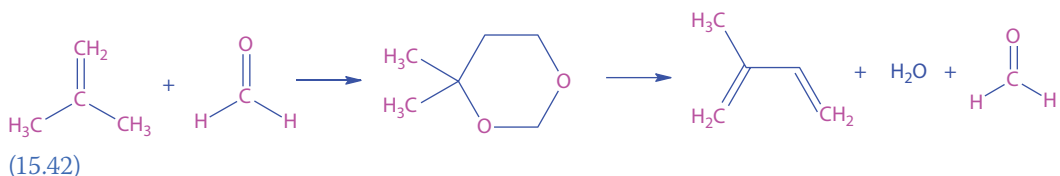


While butadiene is produced as a by-product of the steam cracking process used in the production of ethylene and other olefins in the United States, Europe, and Japan, it is produced in other parts of the world from ethanol, a green material. In the single-step process, ethanol is converted to butadiene, hydrogen, and water through passing the ethanol over metal oxide catalysts. In a two-step process, ethanol is oxidized to acetaldehyde that then reacts with additional ethanol producing butadiene.

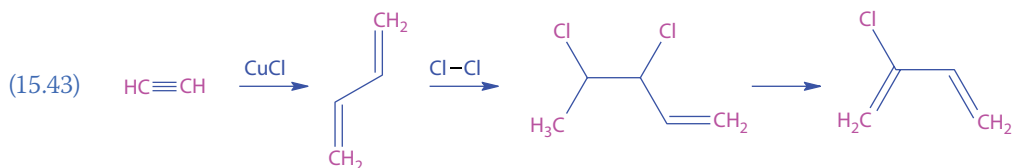
The isoprene monomer is not readily available from direct cracking processes. Several routes are employed for its synthesis. One route begins with the extraction of isoamylene fractions from catalytically cracked gasoline streams. Isoprene is produced by subsequent catalytic dehydrogenation (Equation 15.41).



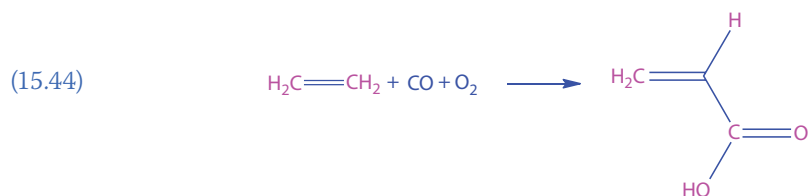
Dimerization of propylene is also used to produce isoprene. Several steps are involved. Initially, dimerization of propylene to 2-methyl-1-pentene occurs. Then isomerization to 2-methyl-2-pentene is affected. Finally, the 2-methyl-2-pentene is pyrolyzed to isoprene and methane. Another multistep synthesis starts with acetylene and acetone. Perhaps, the most attractive route involves formaldehyde and isobutylene (Equation 15.42).



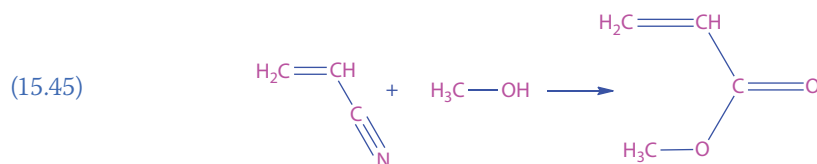
Chloroprene, used for the production of neoprene rubber, is obtained by the dehydrochlorination of dichlorobutene (Equation 15.43). The latter is produced by the chlorination of 1,3-butadiene, which, in turn, is synthesized from acetylene.



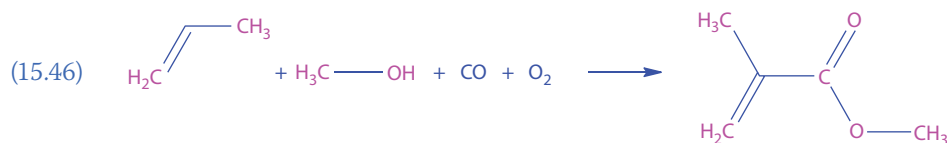
Acrylic acid can be prepared by the catalytic oxidative carbonylation of ethylene or by heating formaldehyde and acetic acid in the presence of KOH (Equation 15.44).



Methyl acrylate may be obtained by the addition of methanol to the reactants in the previous synthesis (15.44) for acrylic acid or by the methanolysis of acrylonitrile:



Methyl methacrylate may be prepared by the catalytic oxidative carbonylation of propylene in the presence of methanol (Equation 15.46).



Most production employs acetone and hydrogen cyanide as the beginning materials. The intermediate cyanohydrin is converted through reaction with sulfuric acid to give a sulfate ester of the methacrylamide. This sulfate ester is subsequently hydrolyzed giving ammonium bisulfate and methyl methacrylate.

A newer process employs ethylene, carbon monoxide, and methanol passed over a catalyst to produce methyl propionate. The methyl propionate is combined with formaldehyde producing (green chemistry) water and methyl methacrylate.

The evolution of the synthesis of feedstocks and monomers continues. It is a testament to the creativeness of scientists. Advances were often opportunities for application of basic chemistry creating a better understanding of the factors that drive chemical reactions. Factors including availability of starting materials, safety, intercorrelation between by-products and other reactions, and sustainability are major considerations. The textbook *Organic Chemistry: Principles and Industrial Practice*, by Mark Green and Harold Wittcoff, Wiley-VCH, NY, 2003, details some of this adventure and is highly recommended to those interested in this subject.

15.4 SEARCH FOR LESS EXPENSIVE FEEDSTOCKS

There is a hunt on for both more and less expensive feedstocks. The United States is now among the largest petroleum-rich countries, thanks to opening up and creating safer techniques to reclaim natural gas, methane, from oil shale. Years ago when hunting for rocks, in the West, we would be in areas where we believed no one else, in recorded history, had been. But we would run across pipes run into the ground locating both oil shale and other petroleum products. The major production of natural gas from oil shale waited for several factors including safer techniques for reclaiming the gas, feedstock stream allowing the use of much larger amounts of natural gas, and a higher price for natural gas. All of these are present today.

Another emerging area where less expensive feedstock research is active involves natural renewable resources. With research focusing on use of celluloses and related materials for production of both monomeric and polymeric materials, there is a major effort aimed and creation of viable and economically feasible feedstocks. Some of the efforts are aimed at creating plants

TABLE 15.2 Growth of Cellulose-Intense Renewable Resources

Material	Type	Land-Use Impact	Yield (Dry Ton/Acre; Average)	CO ₂ Emission (kg/Million BTU) ^a	Region
Corn (cobs, leaves, stock)	Agricultural field waste	None	1–3	25	Midwest
Poplar, hybrid	Rapid growing hardwood	Small	10	10	Most of the USA
Sorghum grain	Livestock feed	Variable	3–4	50	Hot, dry Midwestern plains
Giant reed (<i>Arundo donax</i>)	Grass (perennial)	Unknown	15	10	Southeast
Napier grass (<i>Pennisetum purpureum</i>)	Bunchgrass (perennial)	Displace known crops as cotton, alfalfa	15	20	Southeast
Energy cane (hybrid <i>Saccharum officinarum</i> and <i>S. spontaneum</i>)	Grass (perennial)	Displace known crops as cotton, alfalfa	10–20	15	Southern USA
Switchgrass (perennial bunchgrass)	Bunchgrass (perennial)	Displaces known crops as soybeans, wheat	5	15	Upper Midwest

Source: C&EN, 91(32): *Seeking biomass feedstocks that can compete*, Washington, DC, pp. 11–15, August 12, 2013.

^a For comparison, gasoline creates about 100 kg CO₂/million BTU, sugarcane ethanol 45 kg CO₂/million BTU, and corn ethanol 60 kg CO₂ for million BTU.

that can grow on otherwise low use land such as the dry agricultural land in the West, while other efforts focus on already producing areas where double duty can be done such as creating a food crop like corn and then utilizing the “waste” from the corn stock as a viable feedstock. These feedstocks are being studied as both sources for polymer-related and ethanol-producing materials. Table 15.2 contains some of the candidates. Others will enter the fray and some will be eliminated.

Currently, considering only energy production, natural grass is the least expensive feedstock followed by crude oil and the most expensive of the “big three,” corn. The competition will increase in intensity.

The means to convert these biomasses into feedstocks will vary. Currently, most are looking to employ specially designed microbes, mainly bacteria for the conversion, but enzymes are being developed that will allow more precise conversions.

SUMMARY

1. Feedstocks for the synthesis of monomers of basic polymeric materials must be readily available and inexpensive because they are utilized in polymer synthesis in large quantities, allowing the polymeric materials to be inexpensive. Basic feedstocks today are largely petrochemical and coal-based.
2. Monomer synthesis is both an art and science developed by major and ongoing research efforts allowing the inexpensive and safe availability of the starting materials upon which the polymer industry is based. Commercial monomer synthesis is based on both the availability of inexpensive materials and on an “interconsecutiveness” between products and synthetic by-products that are essential to the synthesis of other essential materials.
3. The precise conditions of synthesis are continually being refined. They are based on “high” science.
4. There is an increased emphasis on green chemistry in the production of monomers.

GLOSSARY

Cannizzaro reaction: An internal oxidation-reduction reaction of aldehydes.

Carbamide: Urea.

Carcinogenic: Cancer causing.

Chemurgic compound: Compound made from a plant source.

Friedel–Crafts condensation: Condensation that takes place in the presence of a Lewis acid such as aluminum chloride.

Grignard reagent: RMgX .

Raney nickel: A porous nickel catalyst produced from a nickel–aluminum alloy.

EXERCISES

- Why are there so many methods for the preparation of adipic acid?
- Write equations for the industrial synthesis of the following:
 - Adipic acid
 - Hexamethylenediamine
 - Sebacic acid
 - Terephthalic acid
 - Maleic anhydride
 - ϵ -Caprolactam
 - Ethylene glycol
 - Glycerol
 - Pentaerythritol
 - TDI
 - Hexamethylenetetramine
 - Phenol
 - Urea
 - Melamine
 - Bisphenol A
 - Epichlorohydrin
 - Methyltrichlorosilane
 - Styrene
 - Vinyl chloride
 - Vinyl acetate
 - Acrylonitrile
 - Vinyl ethyl ether
 - Methyl methacrylate
- Name a reactant or monomer produced by the following:
 - Grignard reaction
 - Friedel–Crafts reaction
 - Beckman rearrangement
 - A chemurgic process
 - A crossed Cannizzaro reaction
- Name three monomers whose synthesis illustrates green chemistry.

FURTHER READING

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Polymer Technology

Today, nearly 10,000 American companies are active in the general area of synthetic polymers. Following is a brief description of these companies divided according to their function.

Manufacturers: There are over 200 major manufacturers of general-purpose polymers and numerous other manufacturers of specialty polymers.

Processors: Some companies manufacture their own polymeric materials for subsequent processing, but the majority purchase the necessary polymeric materials from other companies. Processors may specialize in the use of selected polymers, such as nylons and polycarbonates, or focus on particular techniques of processing, such as coatings, films, sheets, laminates, and bulk molded and reinforced plastics.

Fabricators and finishers: The majority of companies are involved in the fabrication and finishing of polymers, that is, production of the end products for industrial and general public consumption. Fabrication can be divided into three broad areas: machining, forming, and fashioning. Machining includes grinding, sawing, screwing, and other techniques. Forming includes molding and other methods of shaping and joining by welding, gluing, screwing, and other techniques. Fashioning includes cutting, sewing, sheeting, and sealing. Fabrication sequences vary with the polymeric material and desired end product.

Polymer is often sent in the form of small pellets (Picture 16.1) for processing and fabrication.

While much classic polymer technology was developed without the benefit of science, modern polymer technology and polymer science are closely associated. The technology of fibers, elastomers, coatings, composites, drug delivery, and plastics is discussed in this chapter.

Chemistry is moving center stage in many areas of medicine, biology, engineering, environmental science, and physics. While solid-state physics is traditionally based on silicon, polymers offer a much wider vista of opportunities for application and fine-tuning those applications. Some areas are based on single crystals that may be small in our sight, but are large when compared to individual molecules. Even single silicon wafers with a minimum pattern dimension of 200 nm are on the order of 10 times the size of individual molecules. Eventually, electronic, photonic, and stress-strain behavior individuality can be placed into single giant chains creating chains that behave as entire assemblies behave today.

16.1 POLYMER PROCESSING

16.1.1 GENERAL

Polymer processing can be defined as the process whereby raw materials are converted into products of desired shape and properties. Thermoplastic resins are generally supplied as pellets, marbles, or chips of varying sizes, and they may contain some or all of the desired additives. When heated above their T_g , thermoplastic materials soften and flow as viscous liquids that can be shaped using a variety of techniques and then cooled to “lock” in the micro- and gross structure.

Thermosetting feedstocks are normally supplied as meltable and/or flowable prepolymer, oligomers, or lightly or non-cross-linked polymers that are subsequently cross-linked forming the thermoset article.



PICTURE 16.1 Polypropylene pellets with ABS building block pieces added for size perspective.

The processing operation can be divided into three general steps—preshaping, shaping, and postshaping. In preshaping, the intent is to produce a material that can be shaped by application of heat and/or pressure. Important considerations include the following:

- Handling of solids and liquids including mixing, low, compaction, and packing
- Softening through application of heat and/or pressure
- Addition and mixing/dispersion of added materials
- Movement of the resin to the shaping apparatus through application of heat and/or pressure and other flow aiding processes
- Removal and recycling of unwanted solvent, unreacted monomer(s), by-products, and waste (flash)

The shaping step may include any one or a combination of the following:

- Die forming (including sheet and film formation, tube and pipe formation, fiber formation, coating, and extrusion)
- Molding and casting
- Secondary shaping (such as film and blow molding, thermoforming)
- Surface treatments (coating and calendering)

Postshaping processes include welding, bonding, fastening, decorating, cutting, milling, drilling, dying, and gluing.

Polymer processing operations can be divided into five broad categories:

- Spinning (generally for fibers)
- Calendering
- Coating
- Molding
- Injection

Table 16.1 lists some of the major shapes produced by each of these processing groups.

Essentially, all of the various processing types utilize computer-assisted design (CAD) and computer-assisted manufacture (CAM). CAD allows the design of a part and incorporates operating conditions to predict behavior of the pieces prior to real operation. CAD also transfers particular designs and design specifications to other computer-operated systems, CAMs, that

TABLE 16.1 Major Forms of Polymer Processing Groupings

Process	Typical Form of Product
Calendering	Films, sheets
Coating	Film
Injection	Solid
Reaction injected	
Reciprocating screw	
Two stage	
Molding	
Blow	Hollow
Displacement	
Extrusion	
Injection/transfer	
Stretch	
Cold solid	
Compression	Solid, hollow
Rotational	Solid, hollow
Thermoforming	Hollow
Transfer	Solid
Spinning	Fibers
Dry	
Gel	
Melt	
Reaction	
Wet	

allow the actual construction of the part or total apparatus. CAM systems operate most modern processing systems, many allowing feedback to influence machine operation.

These computer-directed processes are given a number of different names including 3D printing. They have progressed to the extent that metals, alloys, and mixtures of polymers can be incorporated into the finished product. The assemblies that carry out these processes have gotten smaller and easier to operate and are leading to concerns such as the manufacture of arms that are largely nondetectable by metal detectors.

Processing and performance are interrelated to one another and to additional factors. Jaffe relates these major groups of factors in an interactive diamond given in Figure 16.1. Understanding these factors and their interrelationships becomes increasingly important as the specific performance requirements become more specific. Performance is related to the chemical and physical structure, and to the particular processing performed on the material during its lifetime. The physical structure is a reflection of both the chemical structure and the total history of the synthesis and subsequent exposure of the material to additional forces. These *additional* forces are included under the broad idea of processing and include any influence that contributes to the secondary (and greater) structure—stress—strain, light, chemical, etc. The portion of the diamond relating processing to physical structure encompasses the study of structure–property relationships. A single material may be processed using only a single process somewhat unique to that material (such as liquid crystals) or by a variety of processes (such as polyethylene), where the particular technique is dictated by such factors as end use and cost.

16.1.2 SECONDARY STRUCTURES: MESOPHASES

The primary and secondary structures greatly influence possible processing scenarios. Here, the secondary structure is generally the same as the physical structure and the primary structure is generally the same as the chemical structure. The end properties and uses are governed

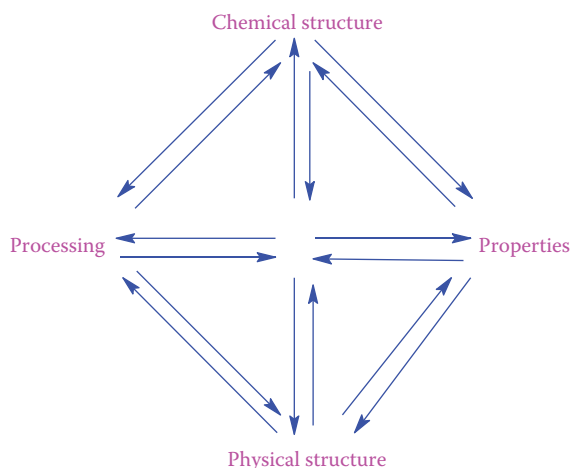


FIGURE 16.1 Relationships that influence the important interrelationships that exist for polymeric materials with respect to processing and end-product properties.

by intrinsic properties that in turn are related to the primary and secondary structures—the chemical and physical structures.

The term “meso” will be used to describe local chain organizations that occur within the nano- and microscale regions (Figure 16.2). While the terms mesophase and meso regions have been employed in describing order within liquid crystals, the definition will be broadened to include other ordered regions within a materials physical or secondary structure. We generally describe polymer secondary structure in simple terms of ordered and/or disordered or crystalline and/or amorphous. The ordered regions can be further described in terms of meso regions or mesophases according to their permanency and ability to influence changes within and about these regions.

Jaffe describes four meso phase classifications. “**Permanent mesogens**” are materials whose microstructures are highly fixed such as in liquid crystalline (LC) polymers. LCs are characterized by highly ordered structures in the quiescent state. They exhibit relatively low viscosities in uniaxial flows and can be easily realigned through application of processing forces such as extrusion. To be processed, such polymers must be in the mesogenic state below their decomposition temperature. This can be achieved through the use of a specific solvent or the introduction of special comonomer units that allow them to melt (or soften), but that are introduced in such a manner as to preserve their LC character. As solids, such materials exhibit high molecular orientation, high tensile moduli (near to theoretical), poor compression (i.e., little unoccupied volume), poor shear behavior, and high tensile strengths (on the order of 4 GPa). Such materials are anisotropic conductors and generally offer good liquid and gas barrier properties. Properties are controlled by the inherent chemical structure, molecular orientation, defect occurrences, and stress transfer mechanisms. Defects often act as the *weak links* in a chain limiting mechanical properties so that defect detection and elimination/curtailment are important and can be dependent on the processing conditions. Only certain processing techniques are suitable.

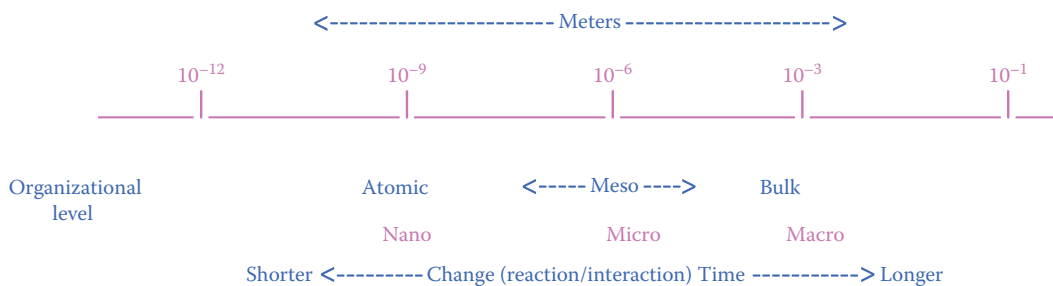


FIGURE 16.2 Relationship between organizational level and size.

“Accessible mesogens” are formed from polymers that are thermotropic (i.e., polymers that have a phase organization that is temperature dependent) but have an accessible isotropic phase below their decomposition temperature. Such polymers can be processed when the material is either in its mesogen or ordered state using LC-type processing forming strong well-ordered products, or at temperatures where the ordered mesogen structure is absent. In temperature-assisted systems, the material is rapidly cooled and quenched, preventing mesogen structure formation producing a metastable isotropic glass or rubber. The metastable material can be processed employing less energy and force followed by a simple annealing and slower cooling that allows the formation of the ordered mesogenic structures along with the appearance of associated properties. Examples of *assembled mesogens* include groups of polymer coils and polymers with side chains that can form such mesogens. In the former case, tertiary-mesophase structures can be formed when the bundles of coiled chains come together.

“Transient mesogens” are regions present in flexible, random coil polymers often caused by application of external forces including simple flowing/shearing. These regions occur through local segmental chain movements that happen within the chain network at points of minimum chain entropy such as sites of entanglements. They are fibrillar-like and appear to be the nucleating phase and key to the shish kebab-like structures in oriented polymer crystals.

These latter groups include many of the so-called crystallites and crystalline regions of common polymers.

Understanding the factors that govern the formation of mesogens will assist in determining the processing conditions for the production of materials with specified amounts, sizes, and distribution of such crystalline microstructures. Mesophases can be local or permeate the entire structure. They can be large or small and present in a random or more ordered arrangement.

16.2 FIBERS

16.2.1 POLYMER PROCESSING: SPINNING AND FIBER PRODUCTION

16.2.1.1 INTRODUCTION

Most polymeric materials are controlled by the Federal Trade Commission (FTC), with respect to the relationship between the name and content including fibers. While the FTC controls industry in the United States, the international standards are generally determined by the International Organization for Standardization (ISO). Table 16.2 contains a brief listing of some of the ISO and FTC names for some of the most utilized fibers.

Fiber production continues to increase for most general groupings.

TABLE 16.2 Generic Names for Synthetic Fibers according to the International Organization for Standardization and Federal Trade Commission

ISO	FTC
Acetate	Acetate
Acrylic	Acrylic
Aramid	Aramid
Chlorofiber	Vinyon/Saran
Cupro/viscose/modal/deacetylated acetate	Cupra/Rayon
Elastane	Spandex
Glass	Glass
Modacrylic	Modacrylic
Nylon/polyamide	Nylon/polyamide
Polyester	Polyester
Polyethylene/polypropylene-Polyolefin olefin	Vinylal/vinal

The dimensions of a filament or yarn are expressed in terms of a unit called the “tex,” which is a measure of the fineness or linear density. One tex is 1 g/1000 m or 10^{-6} kg/m. The tex has replaced denier as a measure of the density of the fiber. One denier is 1 g/9000 m, so 1 denier = 0.1111 tex.

While some natural polymers produce *natural* fibers, fibers from synthetic and regenerated natural polymers are generally produced using one of three spinning processing techniques. These spinning processes are generally employed in the large-scale commercial production of fibers. The first produces fiber from the melted polymer—melt spinning. The other two techniques form fibers from concentrated polymer solutions—dry and wet spinning. Figure 16.3 illustrates the essentials of these three spinning techniques. Table 16.3 lists the most common polymers made into fibers by these three processes.

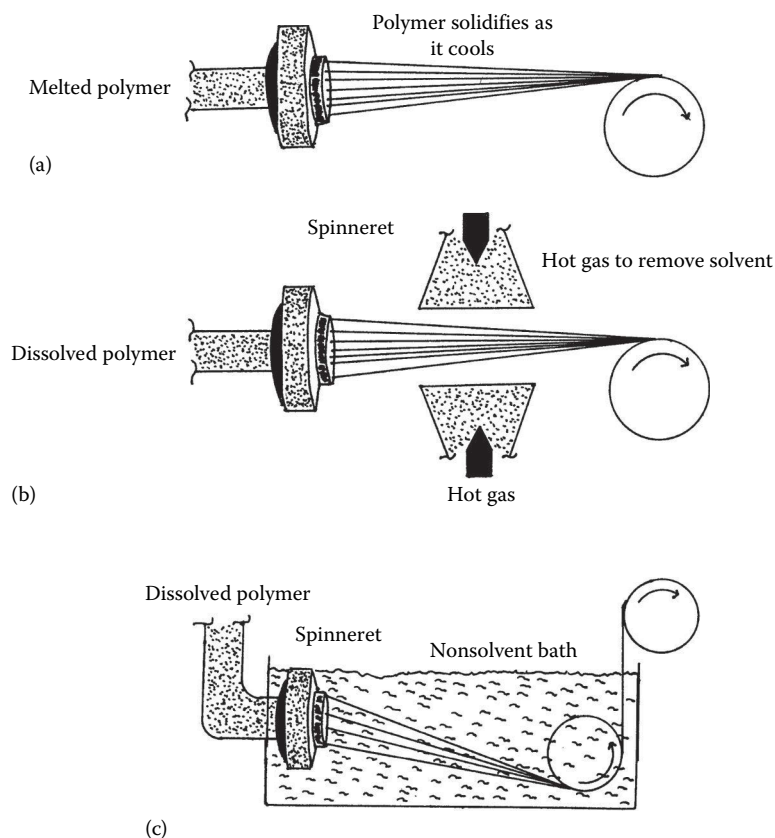


FIGURE 16.3 Fiber production using the three major spinning techniques. (a) Melt spinning, (b) solvent spinning, (c) wet spinning.

TABLE 16.3 (Preferred) Spinning Processes

Melt Spinning	Dry Spinning	Wet Spinning	
		Coagulation	Regeneration
Nylon	Acetate	Acrylic	Viscose
Polyester	Triacetate	Aramid	Cupro
Polyethylene	Acrylic	Elastane/Spandex	
Polypropylene	Elastane/Spandex	Poly(vinyl chloride)	
Poly(vinylene chloride)	Poly(vinyl chloride)		
	Aramid		
	Modacrylic		
	Vinyl		

16.2.1.2 MELT SPINNING

Melt spinning was developed in the 1930s. In melt spinning the polymer is melted or extruded, clarified by filtration, and pumped through a die having one or more small holes. The die is called a spinneret. The number, shape, and size of the hole can vary considerably. The number of holes ranges from several holes to several thousand holes. For continuous filament formation, the number of holes is on the order of 10–100. The exit hole is usually circular giving round fibers. Other shaped holes are also employed that produce fibers with varying shapes.

The extruded fiber is then often uniaxially stretched by take-up rollers rotating at different speeds. The fiber stretching encourages the polymer chains to align on a molecular level producing increased strength in the direction of the pull.

To produce the melted polymer, the polymer chips, rods, marbles, or sheets are heated forming a melted pool of material. In order to minimize oxidation, the melted polymer is blanketed by an inert gas such as nitrogen or argon. The fluidicity (inverse of viscosity) of the melt increases with increased temperature as does the cost to provide the necessary energy and tendency for unwanted reactions to occur. Thus, the polymer melt is generally assisted to and through the spinneret by means of an extruder that may also be used to supply some or all of the heating.

Many nylon and polyester assemblies are configured so that there is a continuous progression from the melt formation of the polymer, and without hardening, the melted polymer is melt spun into fibers.

Monofilament is produced at a lower spinning speed, in comparison with chopped filament, because of the problem of heat buildup within the monofilament. The monofilament is generally cooled by passing it through cold water or by winding it on to a cold quench roll.

16.2.1.3 DRY SPINNING

Polymer concentrations on the order of 20%–40% are employed in dry and wet spinning. In the dry spinning process, the solution is filtered and then forced through a spinneret into a spinning cabinet through which heated air is passed to dry the filament. For economic reasons, the gas is usually air, but inert gases such as nitrogen and superheated water are sometimes used.

Volatile solvents are used to assist in the drying. Water has been used for some systems, such as poly(vinyl alcohol), where the polymer is water soluble. Solvent removal and recycling is important. Spinning is usually carried out using either low (about 1%–2%) or high (10%–50%) solvent in the filament. The amount of solvent influences the drawing process. In high solvent cases, the filaments are plasticized allowing greater extension of the filament and greater alignment of the polymer chains to occur at lower temperatures and lower stresses. The extra solvent is removed just prior to, during, or subsequent to stretching. Just prior to extrusion, the polymer solution is heated to just above the solvent boiling point, increasing the likelihood for ready removal of the solvent.

Dry spinning–produced fibers have lower void concentrations in comparison to melt spun fibers because the presence of solvent molecules causes voids that are often *remembered* by the polymer. This is reflected by greater densities and lower dyeability for the dry spun fibers.

Fibrous glass is the most important inorganic fiber. It is produced by melt spinning in both a continuous filament and staple form. The molten glass is fed directly from the furnace, or melted from rods or marbles, to the spinneret. As the fibrous glass emerges, it is attenuated, quenched, lubricated, and wounded forming a yarn or continuous filament. The temperature for spinning is on the order of 1200°C–1500°C. This temperature is important since it controls the output and, in conjunction with the removal speed, helps control the properties of the resultant fiber including thickness and density.

16.2.1.4 WET SPINNING

Wet spinning is similar to dry spinning except that fiber formation results from the coagulation of the polymer solution as it is introduced into a nonsolvent bath. Since the coagulation process is relatively long, the linear velocity of wet spinning is less than for either melt or dry spinning. Wet spinning allows the placement of holes in the spinneret face to be closer together allowing

productivity to be increased. Even so, it remains the slowest of the traditional spinning processes. The equipment used for wet spinning is similar to that used in dry spinning, though it is not necessary to heat the polymer solution to a high temperature. The spinnerets are immersed in tanks containing the nonsolvent. Wet spinning is the most complex of the three spinning processes, typically including washing, stretching, drying, crimping, finish application, and controlled relaxation, to form tow material. Spinning of natural-derived materials generally includes additional steps including aging or ripening to achieve the desired viscosity and chain length.

Fibers made from wet spinning generally have high void contents in comparison to all of the other processes, giving them increased dyeability. The surface is rougher with longitudinal serrations, and from a round die hole, it has an approximately circular to bean-shaped diameter.

Hollow fibers for gas and liquid separation are prepared by passing air through the material just prior to entrance into the nonsolvent bath.

16.3 ELASTOMERS

Prior to World War II, *Hevea* rubber accounted for over 99% of all elastomers used, but synthetic elastomers account for more than 70% of all rubber used today. Natural rubber and many synthetic elastomers are available in latex form. The latex may be used, as such, for adhering carpet fibers or for dipped articles, such as gloves, but most of the latex is coagulated and the dried coagulant is used for the production of tires and mechanical goods.

Over 5.5 billion pounds of synthetic rubber is produced annually in the United States. The principal elastomer is the copolymer of butadiene (75%) and styrene (25) (styrene–butadiene rubber [SBR]) produced at an annual rate of over 1 million tons by the emulsion polymerization of butadiene and styrene. The copolymer of butadiene and acrylonitrile (Buna-H, nitrile rubber [NBR]) is also produced by the emulsion process at an annual rate of about 200 million pounds. Likewise, neoprene is produced by the emulsion polymerization of chloroprene at an annual rate of over 125,000 tons. Butyl rubber is produced by the low-temperature cationic copolymerization of isobutylene (90%) and isoprene (10%) at an annual rate of about 150,000 tons. Polybutadiene, polyisoprene, and ethylene–propylene (EPM) copolymer rubber are produced by the anionic polymerization of about 600,000, 100,000, and 350,000 tons, respectively. Many other elastomers are also produced.

16.3.1 ELASTOMER PROCESSING

The processing of elastomeric (rubbery) material is quite varied dependent on the end use, form of the material (i.e., dry or in solution), and material processed. Latex forms of rubber can be properly mixed with additives using simple (or more complex) stirring and agitation. The mixing/agitation should be such as to not cause a separation or breakdown of the latex or foam formation. Straight, coagulant, and heat-assisted dipping processes are commonly used to produce a variety of tubes, gloves, etc. Latexes are also used to make thread for the garment industry and adhesives for shoes, carpets, and tape formation.

In the following, we will look at the processing involving bulk rubber. The manufacture of rubber products from this material can be divided into four steps:

1. Mastication
2. Incorporation or compounding
3. Shaping
4. Vulcanization

The shaping and vulcanization steps are combined in a number of processes such as transfer and injection molding or may be separated as in the extrusion and subsequent vulcanization sequence. An outline of these steps is given in Figure 16.4.

We will look at the processing of natural dry rubber first since its processing is similar to other elastomers and because of its historical importance. Natural rubber is a dispersion of rubber

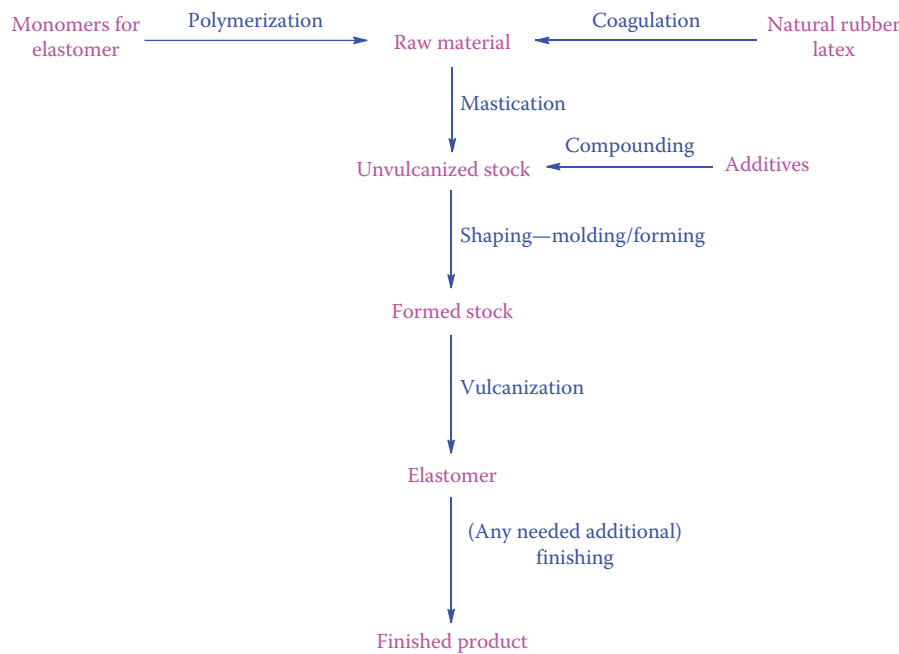


FIGURE 16.4 Outline of steps involved in the processing to form elastomeric materials.

particles in water. Unvulcanized raw rubber obtained by coagulation and drying has large chains with chain lengths on the order of 10^5 carbons.

Mastication is intended to bring the material to the necessary consistency to accept the compounding ingredients. Mastication results in a lowering of chain size to an average chain length on the order of 10^4 carbons. Two basic types of internal mixers are in use. The Banbury has rotors rotating at different speeds creating a *kneading* action such as that employed in handling bread dough. A shearing action between the rotors and the walls of the mixer is also achieved. The Shaw Intermix employs rotors that turn at the same speed and closely intermesh causing an intracomound friction for mixing, thus closely resembling a mill's mixing action.

The next step is the incorporation of various additives—*compounding*. Typical additives include filler, processing aids, activators, processing aids, age resistors, sulfur, antioxidants and antiozone compounds, extenders, plasticizers, blowing agents, pigments, and accelerators.

An important aspect in the compounding is the amount of crystallization of the rubber. If the rubber is in a highly crystalline state, it will mix poorly if at all. Thus, partially crystallized rubber must be heated before it will yield to mixing.

Stabilizers are materials that help the rubber withstand oxidative aging and ozone attack. They act by intercepting the active free radicals breaking the free-radical-associated degradation process. Amines and phenols are generally employed. Reinforcing fillers, of which carbon black is the most important, are added to improve the mechanical properties such as hardness, abrasion resistance, modulus, and tear resistance. It is believed that the rubber adheres to the carbon surface. Carbon black also helps in retarding UV degradation and increases the electrical conductivity, reducing triboelectric charging and acting as an antistatic material.

Natural rubber can be compounded without fillers to give a vulcanized material with high elongation (to about 800%) and high tensile strength (about 28 MPa).

The internal mixers fragment the large rubber molecules by high shear forces. Depending on the particular assembly and ingredients, the created free radicals can combine to give larger molecules or may form smaller chains. Breakdown is often assisted by the use of chemical peptizers such as thiophenols, mixtures of salts of saturated fatty acids, and aromatic disulfides. The fatty acids mainly act as dispersing agents and processing aids.

The viscous prerubber is now *shaped* by addition to a mold of the desired shape. Addition can be achieved by simply pouring the material into the mold, but usually the material is added to the mold employing the usual molding addition (extrusion, compression, and transfer) techniques.

The material can also be treated using most of the other *thermoplastic* processing techniques such as calendering, coating, and extrusion.

The material is now heated to cure, set, or *vulcanize* (all terms are appropriate) the material into the (typically) finished shape. Between one and five percent of sulfur (by weight) is added in typical black rubber mixes giving a vulcanized material with an average of about 500 carbon atoms between cross-links. Larger amounts of sulfur will give a tougher material eventually giving a somewhat brittle, but quite strong, ebonite as the amount of sulfur is increased to about 40%. Sometimes additional finishing may be desirable including painting, machining, grinding, and cutting.

These steps are typical for most of the synthetic elastomers. The use of sulfur for vulcanization is common for the production of most elastomers. Magnesium and zinc oxides are often used for the cross-linking of polychloroprene, CR. Saturated materials such as EPM and fluoroelastomers are cross-linked using typical organic cross-linking agents such as peroxides.

Carbon black is widely used as a reinforcing agent for most synthetic elastomers. Carbon black is especially important for synthetic elastomers such as SBR, NBR, and polybutadiene that do not crystallize at high strains. Thus, non-carbon-filled SBR has a tensile strength of about 2 MPa, and with addition of carbon black, this increases to about 20 MPa.

The processing mentioned previously applies to the processing of typical bulk carbon backbone-intensive elastomers. Other important classes of elastomers are also available. Polyurethanes represent a broad range of elastomeric materials. Most polyurethanes are either hydroxyl or isocyanate terminated. Three groups of urethane elastomers are commercially produced. Millable elastomers are produced from the curing of the isocyanate group using trifunctional glycols. These elastomers are made from high polymers made by the chain extension of the polyurethane through reaction of the terminal isocyanate groups with a polyether or polyester. Low-molecular-weight isocyanate-terminated polyurethanes are cured through a combination of chain extension by reaction with a hydroxyl-terminated polyether or polyester and trifunctional glycols giving cast elastomers. Thermoplastic elastomers are block copolymers formed from the reaction of isocyanate-terminated polyurethanes with hydroxyl-terminated polyethers or polyesters. These are generally processed as thermoplastic materials as are the thermoplastic elastomers. Many of these materials have little or no chemical cross-linking. The elastomeric behavior is due to the presence of physical hard domains that act as cross-links. Thus, SBR consists of soft butadiene blocks sandwiched between polystyrene (PS) hard blocks. These hard blocks also act as a well-dispersed fine particle reinforcing material increasing the tensile strength and modulus. The effectiveness of these hard blocks greatly decreases above the T_g (about 100°C) of PS.

Polysiloxanes (silicons) form another group of important elastomers. Again, processing typically does not involve either carbon black or sulfur.

16.4 FILMS AND SHEETS

Films, such as regenerated cellulose (cellophane), are produced by precipitating a polymeric solution after it has passed through a slit die. Other films, such as cellulose acetate, are cast from a solution of the polymers, but most films are produced by the extrusion process. Some relatively thick films and coextruded films are extruded through a flat slit die, but most thermoplastic films, such as PE film, are produced by air blowing of a warm extruded tube as it emerges from a circular die. Films and sheets are also produced employing calendering. Calendering is also used to apply coatings to textiles or other supporting materials.

The most widely used films are LDPE, cellophane, poly(ethylene terephthalate) (PET), PVC, cellulose acetate, polyfluorocarbons, nylons, polypropylene (PP), PS, and linear low-density polyethylene. The strength of many films is improved by biaxial orientation, stretching. Most of the thermoplastics used as films may also be extruded as relatively thick sheets. These sheets may also be produced by pressing a stack of film at elevated temperature (laminating), or by the calendering process.

Wire is coated by being passed through a plastic extruder, but most materials are coated from solutions, emulsions, or hot powders. The classic brushing process has been replaced by roll coating, spraying, and hot powder coating. The application of polymers from water

dispersions to large objects, such as automobile frames, has been improved by electrodeposition of the polymer onto the metal surface.

Printing inks are highly filled solutions of resins. The classic printing inks were drying oil-based systems, but the trend in this almost billion dollar business is toward solvent-free inks.

16.4.1 CALENDERING

Calendering is simply the squeezing or extruding of a material between pairs of corotating, parallel rollers to form films and sheets. It is used to mix and impregnate fibers into slightly melted matrix material forming impregnated composite tapes, to combine sheets of impregnated paper and fiber woven and nonwoven mats forming laminar composite materials, and, in conjunction with other processing techniques such as extrusion forming films from extruded material, to coat, seal, laminate, sandwich, finish, and emboss.

Because of the variation in flexibility, the terms film and sheet vary with materials. For PVC, films have a thickness of 6 mils (0.15 mm) and less while sheets are thicker than this. While PVC is relatively rigid with a tensile modulus greater than about 690 MPa (105 psi), thin films are easily folded. Films are generally shipped as rolls with the PVC rolled about a central rigid core. Sheets are generally shipped as flat layered sheets.

Films and thin sheets are typically drawn to impart additional unidimensional strength. For films, both unidirectional and bidirectional drawings are used.

16.5 POLYMERIC FOAMS

Prior to 1920, the only flexible foam available was the natural sponge, but chemically foamed rubber and mechanically foamed rubber latex were introduced prior to World War II. These foams may consist of discrete unit cells (unicellular, closed cell), or they may be composed of interconnecting cells (multicellular, open cells) depending on the viscosity of the system at the time the blowing agent is introduced. Over 1.5 million tons of foamed plastic is produced annually in the United States.

Unicellular foams are used for insulation, buoyancy, and flotation applications, while multicellular foams are used for upholstery, carpet backing, and laminated textiles. Expanded PS, which is produced by the extrusion of PS beads containing a volatile liquid, is used to produce low-density moldings such as foamed drinking cups and insulation board. Foamed products are also produced from PVC, LDPE, urea resins, ABS, and PU. PU foams are versatile materials, which range from hard (rigid) to soft (flexible). These are produced by the reaction of a polyol and a diisocyanate.

16.6 REINFORCED PLASTICS (COMPOSITES) AND LAMINATES

16.6.1 COMPOSITES

Theoretical and material considerations for composites are dealt with in Sections 14.2 and 14.3. Here, we will focus more on processing considerations.

Composites are generally composed of two phases, one called the “continuous” or “matrix phase” that surrounds the second called the “discontinuous” or “dispersed phase.” There are a variety of polymer-intense composites that can be classified as shown in Figure 16.5. Many of these composite groups are used in combination with other materials including different types of composites and types of composites except differing in orientation.

Many naturally occurring materials such as wood are reinforced composites consisting of a resinous continuous phase and a discontinuous fibrous reinforcing phase.

The modern ski is a good example of the use of composites to make a product with unique properties (Figure 16.6). The top and sides are composed of ABS polymer that has a low T_g , allowing it to remain flexible even at low temperatures. It is employed for cosmetic and containment purposes.

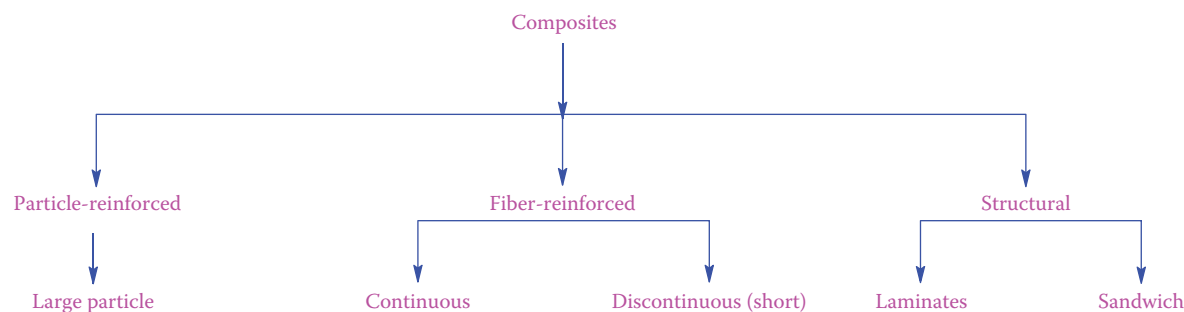


FIGURE 16.5 Classification of polymer-intense composites.

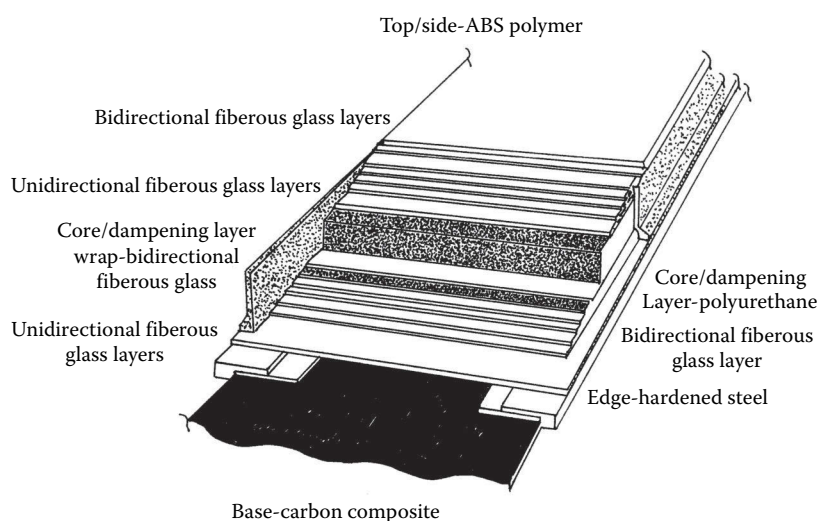


FIGURE 16.6 Cutaway illustration of a modern ski.

Polyurethane forms the core and a damping layer that acts as a filler and improves chatter resistance. The base is a carbon-impregnated matrix composite that is hard, strong, and has good abrasion resistance. There are numerous layers of fibrous glass that are a mixture of bidirectional layers that provide torsional stiffness and unidirectional layers that provide longitudinal stiffness with bidirectional layers of fiberglass acting as outer layers to the polyurethane layers composing a torsional box. The only major noncomposite material is the hardened steel edge that assists in turning by cutting into the ice. These materials work together to give a light, flexible, shock-absorbing, tough ski.

Composites are also used extensively where light, but very strong materials, are needed such as in the construction of the new Boeing 767 where composites play a critical role in the construction of the exterior (Figure 16.7).

Here we will briefly look at each of the main groupings of composites.

16.6.2 PARTICLE-REINFORCED COMPOSITES: LARGE-PARTICLE COMPOSITES

Some materials to which fillers have been added can be considered as composites. These include a number of the so-called cements including concrete (Section 10.2). As long as the added particles are relatively small, of roughly the same size, and evenly distributed throughout the mixture, there can be a reinforcing effect. The major materials in Portland cement concrete are the Portland cement, a fine aggregate (sand), coarse aggregate (gravel and small rocks), and water. The aggregate particles act as inexpensive fillers. The water is also inexpensive. The relatively expensive material is the Portland cement. Good strength is gained by having a mixture of these

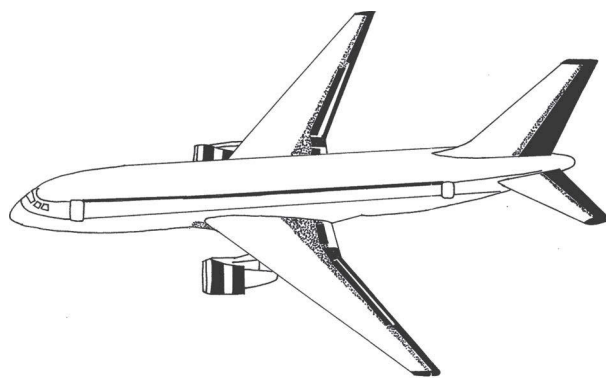


FIGURE 16.7 Use of graphite (solid) and graphite/Kevlar (TM) (dotted) composites in the exterior of the Boeing 767 passenger jet. Sites include wing tips, fixed trailing edge panels, inboard and outboard spoilers, and inboard and outboard ailerons for the large wings and for the tail wings, the fin tip, rudder, elevators, stabilizer tips, and fin fixed trailing edge panels.

such that there is a dense packing of the aggregates and good interfacial contact, both achieved by having a mixture of aggregate sizes—thus the use of large gravel and small sand. The sand helps fill the voids between the various larger gravel particles. Mixing and contact is achieved with the correct amount of water. Enough water must be present to allow a wetting of the surfaces to occur along with providing some of the reactants for the setting up of the cement. Too much water creates large voids and weakens the concrete.

16.6.3 FIBER-REINFORCED COMPOSITES

Mathematically the critical fiber length necessary for effective strengthening and stiffening can be described as follows.

$$\text{Critical fiber length} = [\text{Ultimate or tensile strength times fiber diameter}/2] \text{ times the fiber-matrix bond strength OR the shear yield strength of the matrix—whichever is smaller}$$

Fibers where the fiber length is greater than this critical fiber length are called “continuous fibers” while those that are less than this critical length are called “discontinuous” or “short fibers.” Little transference of stress and thus little reinforcement is achieved for short fibers. Thus, fibers whose lengths exceed the critical fiber length are used.

Fibers can be divided according to their diameters. Whiskers are very thin single crystals that have large length to diameter ratios. They have a high degree of crystalline perfection and are essentially flaw-free. They are some of the strongest materials known. Whisker materials include graphite, silicon carbide, aluminum oxide, and silicon nitride. Fine wires of tungsten, steel, and molybdenum are also used, but here, even though they are fine relatively to other metal wires, they have large diameters. The most used fibers are *organic fibers*, which are either crystalline or amorphous or semicrystalline with small diameters.

16.6.4 PROCESSING OF FIBER-REINFORCED COMPOSITES

There exist a wide variety of particular operations, but briefly they can be described in terms of filament winding, preimpregnation of the fiber with the partially cured resin, and pultrusion. Pultrusion is used to produce rods, tubes, beams, etc., with continuous fibers that have a constant cross-sectional shape. The fiber (as a continuous fiber bundle, weave, or tow) is impregnated with a thermosetting resin and pulled through a die that shapes and establishes the fiber to resin ratio. This stock is then pulled through a curing die that can machine or cut producing the final shape such as filled and hollow tubes and sheets.

The term used for continuous fiber reinforcement preimpregnation with a polymer resin that is only partially cured is “prepreg.” Prepreg material is generally delivered to the customer in the form of a tape. The customer then molds and forms the tape material into the desired shape, finally curing the material without having to add any additional resin. Preparation of the prepreg can be carried out using a calendering process. Briefly, fiber from many spools is sandwiched and pressed between sheets of heated resin with the resin heated to allow impregnation but not so high as to be very fluid.

Thus, the fiber is impregnated in the partially cured resin. Depending upon the assembly, the fiber is usually unidirectional, but can be made so that the fibers are bidirectional or some other combination. The process of fitting the prepreg into, generally onto, the mold is called “lay-up.” Generally, a number of layers of prepreg are used. The lay-up may be done by hand, called hand lay-up, or done automatically, or some combination of automatic and hand lay-up. As expected, hand lay-up is more costly but is needed where one-of-a-kind products are produced.

In *filament winding*, the fiber is wound to form a desired pattern, usually but not necessarily hollow and cylindrical. The fiber is passed through the resin and then spun onto a mandrel. After the desired number of layers of fiber is added, it is cured. Prepregs can be filament wound. With the advent of new machinery, complex shapes and designs of the filament can be readily wound.

16.6.5 STRUCTURAL COMPOSITES

Structural composites can be combinations of homogeneous and composite materials. Laminar composites are composed of 2D sheets that generally have a preferred high-strength direction. The layers are stacked so that the preferred high-strength directions are different, generally at right angles to one another. The composition is held together by a resin. This resin can be applied as simply an adhesive to the various surfaces of the individual sheets, or the sheet can be soaked in the resin prior to laying the sheets together. In either case, the bonding is usually of a physical type. Plywood is an example of a laminar composite. Laminar fibrous glass sheets are included as part of the modern ski construction. These fibrous glass sheets are fiber-reinforced composites used together as laminar composites.

Laminar materials are produced by a variety of techniques. Coextrusion blow molding produces a number of common food containers that consist of multilayers such as layers consisting of PP/adhesive/poly(vinyl alcohol)/adhesive/PP.

Sandwich composites are combinations where a central core(s) is generally surrounded by stronger outer layers. Sandwich composites are present in the modern ski and in high-temperature-stable materials used in the space program. Some cores are very light acting something like filler with respect to high strength, with the strength provided by the outer panels. Simple corrugated cardboard is an example of a honeycomb core sandwich structure except that the outer paper-intense layers are not particularly strong. Even in the case of similar polyethylene and PP corrugated structures, the outer layers are not appreciatively stronger than the inner layer. In these cases the combination acts to give a lightweight somewhat strong combination, but they are not truly composites but simply exploit a common construction.

16.6.6 LAMINATING

Laminating is a simple binding together of different layers of materials. The binding materials are often thermosetting plastics and resins. The materials to be bound together can be paper, cloth, wood, or fibrous glass. These are often referred to as the reinforcing materials. Typically, sheets, impregnated by a binding material, are stacked between highly polished metal plates, subjected to high pressure and heat in a hydraulic press producing a bonded product, which may be subsequently treated, depending on its final use (Figure 16.8a). The end product may be flat, rod shaped, tubular, rounded, or some other formed shape.

Reinforced plastics differ from high-pressure laminates in that little or no pressure is employed. For instance, in making formed shapes, impregnated reinforcing material is cut to a desired shape, the various layers are added to a mold, and the molding is completed by heating

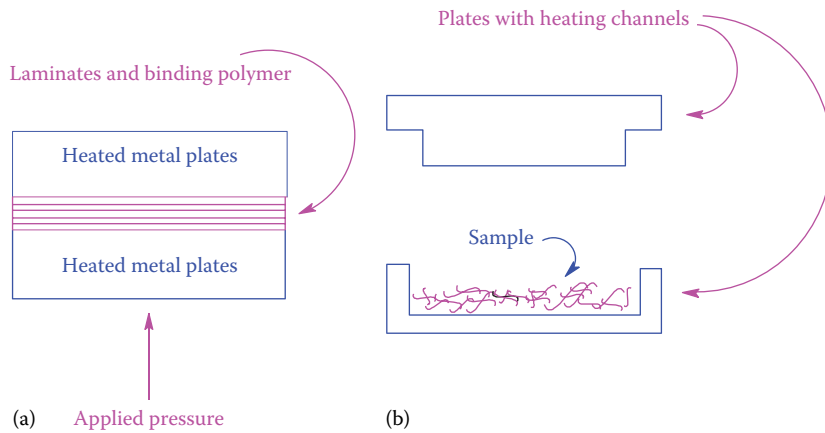


FIGURE 16.8 Assembly employed for the fabrication of laminates (a) and reinforced plastics (b).



PICTURE 16.2 Laminate impregnated material as classroom desktops.

the mold (Figure 16.8b). This process is favored over the high-pressure process because of the use of a simpler, lower cost mold and production of strain-free products.

Commercially there are a number of important laminates including plywood and Formica. Formica was invented in 1912 by Daniel O'Connor and Herbert Faber while working at Westinghouse. Their original idea was to find a substitute for mica, thus its name. Formica laminates now refer to decorative products composed of several layers of paper impregnated with melamine resin or other suitable resin. While in the 1940s–1990s most kitchens and bathrooms had Formica tops, today these tops are made from stone or solid resin. But Formica coverings are still popular as tops of student desks (Picture 16.2) and other furniture tops.

16.7 MOLDING

Molding is a general technique that can be used with plastics and thermosetting materials when employing mobile prepolymer. Molding is used to produce sheetlike, foamed, hollow, or solid materials from very small to very large objects. Here, we will look at various molding processes.

16.7.1 INJECTION MOLDING

The most widely employed processing techniques for thermoplastics are extrusion and injection molding. Injection molding is also used to produce some thermoset products utilizing fluid prepolymer.

Injection molding involves forcing, injecting, a molten polymer into a mold and when it cools, it becomes solid. The mold separates allowing the molded material to be released. The mold parts are again joined and the process begins again.

Injection molding allows the rapid, economical production of small to large parts. It provides close tolerances, and the same machine can be used to mold many different articles. Parts can be molded combining the polymer with other polymers and with any number of additives. Further, it can be run so that various parts can be easily married as part of an entire or combined part production assembly of an article. The ability to easily modify the operating conditions of the injection molding machine is important because of the variety of articles that may be needed, variety of material employed to produce the same (general) article, variety of materials to produce different injection-molded articles, and the variability of supposedly the same polymer material from batch to batch.

Injection molding is not new. A patent was issued in 1872 for an injection molding machine for camphor-plasticized cellulose nitrate, celluloid. Almost all of the machines used today are reciprocating or two-stage screw types. Both types employ a reciprocating Archimedean-like screw similar to that of a screw extruder. A few are of the plunger type.

A traditional injection apparatus consists of a hopper, which feeds the molding powder to a heated cylinder where the polymer is melted and forced forward by a reciprocating plunger or screw. The cooled part is ejected when the mold opens and then the cycle is repeated. The molten material passes from the nozzle through a tapered sprue, a channel or runner, and a small gate into the cooled mold cavity. The polymer in the mold is easily broken off at the gate site, and the materials in the sprue, runner, and gate are ground and remolded. An illustration of such an injection molding press is given in Figure 16.9. The hopper (a) feeds the molding powder to a heated cylinder (b) where the polymer is melted and forced forward by a reciprocating plunger (c) or screw. The molten material advances toward a spreader or torpedo into a cool, closed, (here) two-piece mold (d). The cooled part is ejected when the mold opens and then the cycle is repeated. The molten plastic is passed from the nozzle through a tapered sprue, runner, and a small gate into the cooled mold cavity. The plastic in the narrow gate section is easily broken off and excess material remaining within the sprue, runner, and gate ground and is remolded.

In a reciprocating screw machine, the material is collected in front of the screw that continues to move backward as additional material is melted. The area where the melted material is collected corresponds to the heating chamber or pot in a two-stage system. The material is melted by

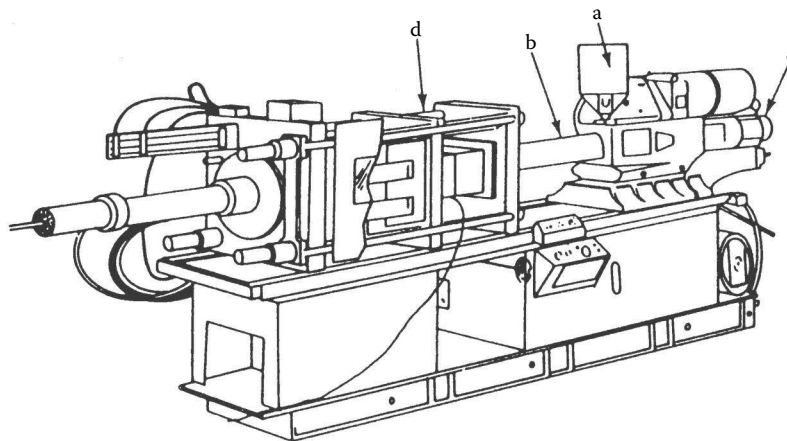


FIGURE 16.9 Cross section of an injection-molding press. (From Seymour, R., *Modern Plastics Technology*, Reston Publishing Co., Reston, VA, 1975.)

the internally generated heat caused by the friction of the polymer segments and chains rubbing against one another. The screw is also good at mixing so that additive introduction and mixing of different polymers can be achieved in the same step with overall polymer melting.

As the size of the molded product becomes larger, it is more difficult to control uniformity and to maintain a sufficient clamping force to keep the mold closed during filling. Reaction injection molding (RIM) overcomes these problems by largely carrying out the polymerization reaction in the mold. The most widely used RIM materials are polyurethane- and polyurethane-reinforced elastomeric materials. Most of the automotive interior panels (such as dashboards) are produced using RIM.

On a molecular level, partially crystalline to amorphous polymers are normally used. As the material is heated, Brownian motion occurs resulting in a more random chain arrangement. When a unidirectional force is applied to a resting polymer melt, the chains tend to move away from the applied force. If the applied force is slow enough to allow the Brownian movement to continue to keep the polymers in a somewhat random conformation, then the movement of the polymer melt is proportional to the applied stress; that is, the flow is Newtonian.

As the rate of movement increases, chain alignment occurs along the direction of flow with movement too fast for the Brownian factors to return the system to a somewhat random state and flow is then non-Newtonian. Most systems are operated, at least at the injection stage, under non-Newtonian conditions so that some polymer alignment occurs. If the polymer melt flow rate continues to increase, polymer chains align parallel to the flow plane and eventually reach a point where it again becomes Newtonian. Even so, the polymer chains have been aligned as the flow processes moved through the non-Newtonian flow range.

As the molten polymer is injected into the cold mold, it rapidly solidifies locking in at least some of the *orientated* chain conformations. As the material enters the cold mold, the flow turbulence occurring with the outermost layers is generally sufficient to result in a more randomized, more amorphous outer structure. As the outermost chains cool, they *drag* the next chains effectively aligning them giving a more ordered structure. Finally, the cooling of the inner material is slowed because of the heat uptake of the outer layers allowing Brownian movement to again somewhat randomize these chains. Thus, the structure of the molded part is varied and can be further varied by controlling the flow rate, cooling rate, and flow and cooling temperatures for a specific injected-produced material.

16.7.2 BLOW MOLDING

Most molded material, as well as most processed material, will have a different surface or skin composition compared with the bulk or core material. Take a look at a common disposable PS foam plate. The surface or skin is smooth. Break it and look at the core, and it is different being more cellular. This difference is greater than having simply a difference in appearance. There also exist different fine molecular-level differences. Molecular structure, and associated bulk properties, is controlled in part by the particular processing and processing particulars.

Blow molding has been used for many years in the creation of glass bottles. In about 1872, the blow molding of thermoplastic objects began by the clamping of two sheets of cellulose nitrate between two mold cavities. Steam was injected between the two sheets softening the sheets and pushing the material against the mold cavities. But, it was not until the late 1950s that large-scale use of blow molding began with the introduction of blow-molded high-density polyethylene (HDPE) articles.

Figure 16.10 contains a sketch of an extrusion blow-molding scheme. Here a heat-softened hollow plastic tube, or parison, is forced against the walls of the mold by air pressure. The sequence of material introduction into the mold and subsequent rejection of the material from the mold is generally rapid and automated. Approximately 1 million tons of thermoplastics is produced by this technique annually.

While there is a wide variety of blow-molding techniques, there are three main blow-molding procedures:

- Injection blow molding that employs injection-molded *test tube*-shaped preforms or parisons

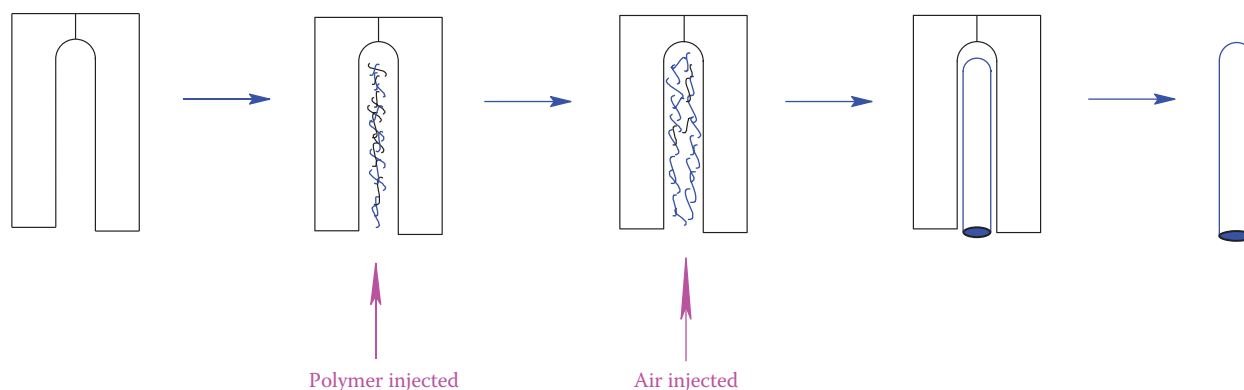


FIGURE 16.10 Steps employed in simple extrusion blow molding of a test tube. From left to right: mold closed, softened material introduced, air or other gases injected forcing the softened thermoplastic against the walls of the mold, and after suitable cooling, the mold is opened giving the molded plastic test tube.

- Extrusion blow molding that uses an extruded tube preform or parison
- Stretch blow molding that employs an injection-molded, extrusion blow-molded, or extruded tube preform

The major difference between injection and extrusion blow molding is the way the soft hollow tube (called a preform or parison) is made. In injection blow molding, two different molds are used. One mold forms the preform, and the other mold is used in the actual blow-molding operation to give the final shaped article. In the molding process, the softened material preform, from the preform mold, is introduced into the blowing mold and blow molded to fit the cavity of the second *finished* blow mold. This process is sometimes also called transfer blow molding because the injected preform is transferred from the preform mold to the final blow mold. This allows better control of the product wall thickness and the thickness of the various curved locations.

Injection blow molding is typically used to produce smaller articles, generally with a total volume of 500 mL or less. Because two molds are used, there is little waste material that must be recycled and there is no bottom weld joint. It allows the production of small articles that at times are very difficult to manufacture in any other way.

Extrusion blow molding is the most common process used to produce hollow articles larger than 250 mL up to about 10,000 L. In extrusion blow molding, the softened material is extruded continuously or intermittently. The preform is introduced, the mold has closed, and air or other gases are introduced, forcing the preform material against the mold surfaces. After cooling, the mold is opened and the formed article rejected. Articles with handles and offset necks can be manufactured using extrusion blow molding. Unlike injection blow molding, waste that must be cut away and recycled is produced as the two halves of the mold are pressed together.

In continuous extrusion blow molding, the preform is continuously produced at the same rate as the article is molded, cooled, and released. To avoid interference with the preform formation, the mold-clamping step must be rapid to capture the preform and move it to the blow mold station. There are various modifications of this that allow essentially continuous operation.

The stretching is best done just above the materials T_g , allowing a balance between good alignment because of ease in chain movement and a decreased tendency to form crystalline areas in the melt allowing ready flow of material.

16.7.3 ROTATIONAL MOLDING

In rotational molding, also known as rotomolding, the mold (or cavity) is filled with material, either as a solid power or liquid. The mold is closed, placed in a heated oven, and then rotated biaxially. The mold is then cooled and opened, and the article recovered. Powders of about 35 mesh

(500 μm) are typical though different sizes are also employed. The distribution of particles and additives is determined by mixing and rotation ratio.

Almost any mold design can be incorporated into rotational molding. Tanks used for agricultural, chemical, and recreational vehicle industries are made using rotational molding as are containers used for packaging and material handling, battery cases, portable toilets, vacuum cleaner housings, light globes, and garbage containers. Rotational molding produces little waste and produces a material with uniform wall thickness as well as strong corner sections.

16.7.4 COMPRESSION AND TRANSFER MOLDING

While there are a number of molding processes, compression and transfer molding are the main techniques for molding articles from thermosetting materials. In compression or transfer molding, the material, thermoplastic or prethermoset material, is heated sufficiently to soften or plasticize the material to allow it to enter the mold cavity. The softened material is held against the mold by pressure. For thermoplastics it is then cooled below the T_g , thus locking in the shape. For thermosets it is held until the cross-linking occurs thereby locking in the article shape.

The most widely employed molding process is compression molding where the material is placed in the bottom half of an open heated mold. The second half of the mold is closed and brings heat and pressure against the material, softening the material further and eventually allowing it to cross-link, if it is a thermoset. When completed, the pressure is released and article removed from the mold. Generally, excess material, or flash, is produced. Figure 16.11 contains a representation of a simple compression molding assembly.

Compression molding is one of the oldest material handling processes. Ancient Chinese employed compression molding to form articles from paper-mache. Rubber articles were made in the early nineteenth century from composites of woody fibers and gum shellac. Baekeland used compression molding to make many of his early phenol–formaldehyde products.

Transfer (or plunger) molding introduces the *to be molded material* through a small opening or gate after the mold is closed (Figure 16.11). This process can be used when additional materials, such as a glass globe or other designed objects, are placed in the mold prior to closing the mold. In true transfer or pot-type molding, the mold is closed and placed in a press. The soften material is introduced into an open port at the top of the mold. The plunger is placed in the pot and the press closed. As the press closes, it pushes against the plunger forcing the molding material into the mold cavity. Excess molding compound is used to ensure that there is sufficient material to fill the mold. After the material is cured and/or cooled, the plunger is removed and the part removed from the mold. In plunger molding, the plunger is part of the press rather than part of the mold. Because of this it can be smaller than the pot-type plunger. The clamping action of the press keeps the mold closed. Here there is less material waste compared with the pot-type molding.

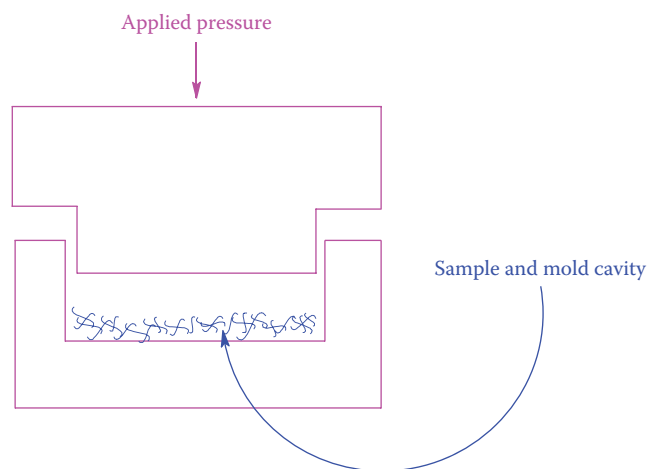


FIGURE 16.11 Representation of a compression molding assembly.

In cold molding, the compound is compacted in a mold at around room temperature. The compressing operation is similar to that employed in the production of KBr pellets from powdered KBr. The compound generally contains a lot of filler and binder. The compacted material is removed from the mold and placed in an oven where it becomes cross-linked. Ceramic materials are often produced using cold molding.

16.7.5 THERMOFORMING

Thermoforming involves heating a sheet or thick film just above its T_g or T_m , stretching it against a rigid mold, cooling, and trimming the formed part. Inexpensive aluminum, wood, epoxy, and steel molds are often employed. This allows the construction of inexpensive molds that allow the production of low-volume articles. All thermoplastic materials that can be formed into sheets can be thermoformed provided that the heating does not exceed the ability of the sheet to support itself.

Thermoforming is employed to convert extruded sheets into smaller items such as packaging containers, plates, trays, bath tubs, pickup truck liners, freezer liners, cabinetry, and cups. The skin packaging that involves a flexible plastic skin drawn tightly over an article on a card backing is made by thermoforming. Thermoforming permits the production of small to large articles including those with thin walls such as drinking cups. Thus, thermoforming is employed to produce articles with a relatively high surface-to-thickness ratio.

Multilayered materials can be readily formed using thermoforming including food packaging that may involve inclusion of layers of ethylene–vinyl alcohol copolymers, PS, polyolefins, and/or copolymers of vinylene dichloride and vinyl chloride.

PS is the most widely used resin material for thermoforming. High-impact PS is the most widely used, being employed largely in the packaging areas including disposables (foam drinking cups, lids, lunch trays, and food service containers), packaging for medical devices, and food packaging (meat and poultry trays, egg cartons, dairy and delicatessen containers, and barrier packages). ABS is thermoformed to produce more durable articles such as refrigerator inner door liners, recreational vehicle and boat parts, automotive panels, picnic coolers, and luggage exteriors. HDPE is used in the manufacture of pickup truck liners, golf cart tops, and sleds. Crystallized PET is used in the thermoforming of food trays that can be heated in a microwave or regular oven. Frozen-food oven-friendly trays are made from coextruded polycarbonate–polyetherimide. Polycarbonates and poly(methyl methacrylate) are thermoformed to produce skylights, windows, tub and shower stalls, and outdoor display signs. Poly(vinyl chloride) is used in the production of blister packaging of pharmaceuticals, foods, cosmetics, and hardware.

16.8 CASTING

Casting is employed in making special shapes, sheets, films, tubes, and rods from both thermoplastic and thermoset materials. The essential difference between most molding processes and casting is that no added pressure is employed in casting. In casting, the polymer or prepolymer is heated to a fluid, poured into a mold, cured at a specific temperature, and removed from the mold. Casting of films and sheets can be done on a wheel or belt or by precipitation. In the case of a wheel or belt, the polymer is spread to the desired thickness onto a moving belt as the temperature is increased. The film is dried and then stripped off. *Drying* may occur through solvent evaporation, polymerization, or cross-linking.

16.9 EXTRUSION

Extrusion involves a number of processing operations and is widely used. We will look at extrusion as it is involved in several of these processes. These processing operations are used together or separately. A representative extruder is shown in Figure 16.12. The extruder accepts granulated thermoplastic in a hopper (c) and forces it from the feed throat (d) through a die (f). The die may

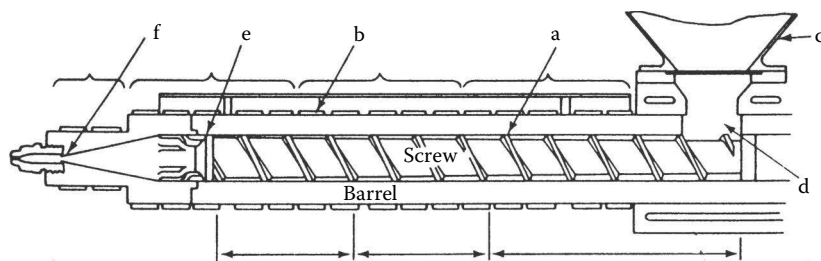


FIGURE 16.12 Sketch details of screw and extruded zones. (From Seymour, R., *Modern Plastics Technology*, Reston Publishing Co., Reston, VA, 1975.)

be circular for the production of a rod or pipe, or flat for the production of a sheet, or it may have any desired profile for the continuous production of almost any uniformly shaped product. The screw (a) advances the polymer through a heated cylinder (barrel) (b) to a breaker plate and protective screen pack (e) before it enters the die (f). The extrusion process may be divided into a feed or transport zone, a compression or transition zone, and a metering zone. Over 1 million tons of extruded pipe is produced annually in the United States.

In extrusion, a fluid material, generally rendered a fluid material through heating, is forced through a shaping device. Since there is a need for quickness and because the preshaped material is quite viscous, extrusion requires high pressure to drive or force the melt through a die. The melts can be extruded as pipes, sheets, films, or molds.

Along with moving and shaping the molten material, extruders also act to disperse additives and are often the agent for creating heat, thus enabling the material to become molten.

16.9.1 PROCESSING

Many different processes are used to apply a thin layer of liquid-melted polymer or polymer solution or dispersion including rollers, spraying, calendering, and brushing. Here we will look at the industrial application of coatings onto film and sheetlike materials. Figure 16.13 contains examples of general coating processes employed to achieve this. The moving sheet is called a web. In *roll coating* (Figure 16.13a), the lower roller picks up the coating material that then transfers it to the second roller and finally to one surface of the mat. Spacing of the rollers, viscosity of the polymer solution in the dip tank, and roller speed and size control the thickness of the applied coating.

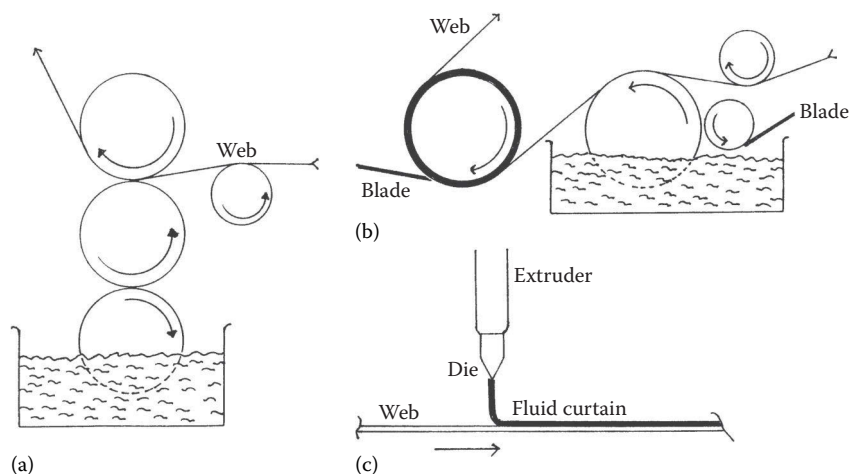


FIGURE 16.13 Three principal industrial coating processes for films and thin sheets. (a) Roll coating, (b) blade coating, and (c) curtain coating.

In *blade coating* (Figure 16.13b), a flexible blade helps control the coating thickness. The blade may be located after the bath or within the bath as part of the roller system. The blade is flexible and adjustable so that the amount of coating material can be controlled by application of force on the blade and/or distance the blade is from the web or roller. Both of these processes are forms of calendaring. The third main coating process involves direct application of the coating material forming a so-called *fluid curtain*, Figure 16.13c. This process, *curtain coating*, is usually used in conjunction with a curing process. The coating thickness is controlled by web speed, polymer concentration, and rate of application from the extruder. Coatings can be divided according to formulation, drying mechanism, or other systems of categorizing. A coating is normally a mixture of various components. For instance, the label on a latex emulsion-type paint might have as major components poly(ethyl acrylate), titanium dioxide as the white pigment, and water. It could also have china clay and calcium carbonate as extenders, carboxymethylcellulose as a colloid thickener, a defoaming agent, a plasticizer, a surfactant dispersing aid, additional coloring agents, and an added fungicide.

The hiding power is a measure of the ability of the coating to achieve a specified degree of *hiding* or obliteration. Industrially, it is often tested by comparing the reflectance of the coated surface overpainting a black surface (i.e., the tested paint applied over a black surface) with white panels. The ability to cover or hide is related to the scattering of incident light hitting the surface and returning to the observer or light meter. As the film surface increases, the ability of light to penetrate the surface coating and be scattered from the (black for tests) undercoating lessens. For a simple white latex paint, no absorption occurs, and we can consider the scattering occurring at the interfaces of the transparent polymer matrix and the dispersed pigment particles. The scattering coefficient of polymers can be obtained from reflectance measurements. While the refractive indices for most polymers do not widely vary (generally about 1.5), the scattering coefficients can vary widely. For good scattering, the refractive index of the polymer should differ from that of the pigment. For instance, while calcium carbonate, with a refractive index of about 1.6, is often used as a pigment in paints, it has a much lower hiding power than titanium dioxide (rutile titanium(IV) oxide), with a refractive index of about 2.8.

Scattering efficiency increases as the pigment surface area becomes larger; thus, smaller particles aid in increasing the scattering to a lower limit determined by the wavelength of light; thereafter, reduced size produces a rapid loss in scattering efficiency. For good scattering, and good hiding power, the particles should be dispersed in a homogeneous manner so that dispersing agents are commonly used.

16.9.2 RAINWEAR

When it rains we grab an umbrella or put on a raincoat. Charles Macintosh is credited with the discovery of waterproof coats, aka raincoats. The first raincoats predated Macintosh's concept by hundreds of years. As early as the thirteenth century, South American Indians coated cloth with natural rubber latex, making waterproof caps and footwear. Latex is a natural rubber, a nonpolar material, and as such it repels polar water molecules. As this latex was shipped to Europe, bacteria attacked the natural rubber, making it useless. In 1748, Francois Fresneau developed a process of dissolving natural rubber in nonpolar turpentine forming a rubber solution that was poured onto fabric rendering it *rainproof*. A contemporary of Macintosh, James Syme found that coal tar naphtha, again a nonpolar liquid, dissolved rubber and could be used to make waterproof fabric. He turned to other ventures rather than commercializing his process.

Coal tar naphtha is a waste by-product from the conversion of coal into gas that was used as the fuel for streetlamps. Macintosh was under contract of the Glasgow Gas Light Company to work with the waste by-products. He was extracting ammonia from the by-products for use in his father's dye business. He was left with unusable coal tar naphtha. So, he looked for uses for this waste solvent. Shortly, he found that it dissolved rubber, which could be poured onto fabric creating waterproofed material. The material remained sticky and had an unpleasant odor. He conquered the problem of tackiness by sandwiching the treated fabric between two other fabric layers. The smell remained. Macintosh patented the idea in 1823, but his rainproof material was not well received, presumably because of the unpleasant odor. Fortunately for him, the military purchased waterproof fabric from him.

Improvements continued making the material lighter, more flexible, and less smelly. Use of cold cure vulcanization where the rubber was treated with sulfur compounds eliminated the *sticky* problem, allowing a single layer of impregnated fabric to be adequate.

Today, there exists a variety of polymeric materials that offer rainproof umbrellas and clothing including *breathable* fabrics. Gore-Tex-derived materials offer a combination of layers including a breathable polymer membrane made of microporous polytetrafluoroethylene under a layer of polyurethane. The polytetrafluoroethylene pores provide a layer of air. The polyurethane has a high diffusivity for water vapor taking away any water that is on the skin, such as water vapor or sweat. The temperature inside the clothing is generally greater than the external temperature and acts as a *driving force* to *push* the water through the polytetrafluoroethylene pores and away from the skin.

16.10 COATINGS

The fundamental purpose for painting is decorating, whereas the purpose for coating is for protection (Pictures 16.3 and 16.4). In truth, we often do not differentiate between the two terms. Government edicts concerning air, water, solid particulates, and worker conditions are having real effects on the coatings industry with the generation of new coating techniques. Paint solvents, in particular, are being looked at in view of increased environmental standards. The volatile organic compound regulations under Titles I and VI of the Clean Air Act specify the phasing out of ozone-depleting chemicals—namely, chlorinated solvents. Baseline solvent emissions are to be decreased. These, and related regulations, affect the emission of all organic volatiles, whether in coatings or other volatile-containing materials.

A major driving force in coatings continues to be a move toward water-based coatings. Another is to eliminate the *odor* of the coating. Most waterborne coatings actually contain about 8%–10% nonaqueous solvent. The odor we get as the coating is drying is mainly due to this solvent evaporating. Work continues to develop the right balance of properties and materials that allow the latex particles to flow together and coalesce into suitable films without the need of nonaqueous liquids.



PICTURE 16.3 Some stores have a wide selection of types of paints. Coloring is typically added.



PICTURE 16.4 Paint colors for decoration.

Another area of active research is the development of paints that dry under extreme or unusual conditions including under water and on cool substrates. The latter allows the painting season for exterior coating to be extended, particularly in the northern states.

Work continues on making more durable exterior paints. Remember that there is a difference in requirements of exterior and interior paints. For instance, interior paints are generally required to be faster drying and more durable against scraps and punctures since it is the inside of the house that generally experiences such traumatic events. By comparison, exterior paints need to remain flexible and adhered under a wide variety of humidity and temperature. A more durable exterior coating should allow it a longer lifetime because it can better withstand stress caused by the pounding of the rain, sticks, and human-afflicted dings and dents. Binders or coating resins are critical to the performance of coatings. They bind the components together. Since the primary cost of most commercial application of coatings is labor, the market will allow price increases for products that give added positive properties. Table 1.8 contains a listing of the production of paints for the year 2009.

Paint manufacturers in the United States sell about 1300 million gallons of coating material annually or about 4 gal for every man, woman, and child. Paint is typically a mixture of a liquid and one or more colorants (pigments). The liquid is called a “**vehicle**” or binder (adhesive) and may include a solvent or thinner along with the coating agent. The colored powders are called “**pigments**,” which may be prime or inert. Prime pigments give the paint its color. These may be inorganic, such as titanium dioxide (titanium(IV) oxide, the most widely used pigment by far) for white (but contained in many colored paints as well); iron oxides for browns, yellows, and reds; or organic compounds such as phthalocyanine for greens and blues. Inert pigments such as clay, talc, calcium carbonate, and magnesium silicate make the paint last longer and may contribute to the protective coating as do mica chips in some latex paints that actually form a clad on drying. The paint may also contain special additives and catalysts. Thus, many paints in wet areas contain an agent to fight fungus, rot, and mold.

Vehicles include liquids such as oils (both natural and modified natural) and resins and water. A latex vehicle is made by suspending synthetic resins, such as poly(ethyl acrylate), in water. This suspension is called an emulsion, and paints using such vehicles are called latex, waterborne, or emulsion paints. When the vehicle comes in contact with air, it dries or evaporates, leaving behind a solid coating. For latexes, the water evaporates, leaving behind a film of the resin.

Paints are specially formulated for specific purposes and locations. Following is a brief description of the most popular paint types.

Oil paints: Oil paints consist of a suspension of pigments in a drying oil, such as linseed oil. The film is formed by a reaction involving atmospheric oxygen, which polymerizes and cross-links the

drying oil. Catalysts may be added to promote the cross-linking reaction. Oil paints, once dried, are no longer soluble, although they can be removed through polymer degradation using the appropriate paint stripper.

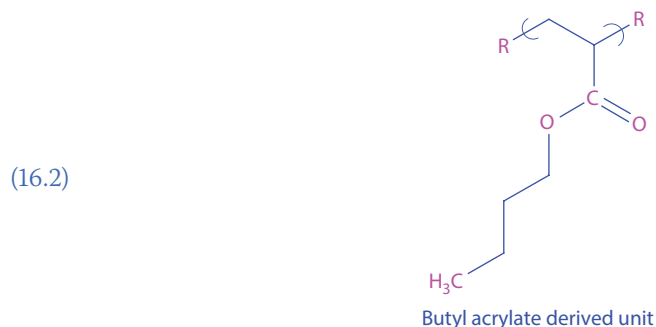
Oil varnishes: Varnish coatings consist of a polymer, either natural or synthetic, dissolved in a drying oil together with appropriate additives as catalysts to promote cross-linking with oxygen. When dried, they produce a clear, tough film. The drying oil is generally incorporated, along with the dissolved polymer, into the coating.

Enamels: Classical enamel is an oil varnish with a pigment added. The added polymer is typically selected to provide a harder, glossier coating than the oil varnish mixture. Today, there are latex enamels that are similar to the oil enamels except no natural oil is present.

Lacquers: Lacquers consist of polymer solutions to which pigments have been added. The film is formed through simple evaporation of the solvent leaving the polymer film as the coating. These coatings are formed without subsequent cross-linking; thus, the surface exhibits poor resistance to some organic solvents.

Latex paints: Latex paints today account for more than one-half of the commercial paint sold. They are characterized by quick drying (generally several minutes to several hours), little odor, and easy cleanup (with water). Latex paints are polymer latexes to which pigments have been added. The film is formed by coalescence of the polymer particles on evaporation of the water. The polymer itself is not water soluble, though these paints are called waterborne coatings.

The composition of latex paints is variable depending on the end use, manufacturer, and intended cost. Ethyl acrylate (16.1) and butyl acrylate (16.2) are frequently employed as the synthetic resin monomer. Most synthetic resins for coatings are copolymers of the acrylics. Vinyl acetate or other monomers are sometimes incorporated.



The T_g of the copolymer must be below the application temperature to allow diffusion of water from the latex to occur as it is drying forming the protective film.

16.11 ADHESIVES

In contrast to coatings, which must adhere to one surface only, adhesives are used to join two surfaces together. Resinous adhesives were used by the Egyptians at least 6000 years ago for bonding ceramic vessels. Other adhesives, such as casein from milk, starch, sugar, and glues from animals and fish, were first used at least 3500 years ago.

Adhesion occurs generally through one or more of the following mechanisms. Mechanical adhesion with interlocking occurs when the adhesive mixture flows about and into two rough substrate faces. This can be likened to a hook and eye, where the stiff plastic hooks get caught in the fuzz-like maze of more flexible fibers. Chemical adhesion is the bonding of primary chemical groups. Specific or secondary adhesion occurs when hydrogen bonding or polar (dipolar) bonding occurs. Viscosity adhesion occurs when movement is restricted simply due to the viscous nature of the adhesive material.

Adhesives can be divided according to the type of delivery of the adhesive or by the type of polymer employed in the adhesive. Following are short summaries of adhesives divided according to these two factors:

Solvent-based adhesives: Solvent-based adhesion occurs through action of the adhesive on the substrate. Solidification occurs on evaporation of the solvent. Bonding is assisted if the solvent partially interacts or, in the case of model airplane glues and PVC piping glues, actually dissolves some of the plastic (the adherent). Thus, model airplane glues and PVC glues often contain volatile solvents that dissolve the plastic, forming what is called a solvent weld. Some of the PVC glues actually contain dissolved PVC to assist in forming a good weld. A major difference between home-use PVC adhesive and industrial PVC adhesive is added color for the commercial adhesive, so building inspectors can rapidly identify that appropriate solvent welding has been accomplished.

Latex adhesives: Latex adhesives are based on polymer latexes and require that the polymers be near their T_g so that they can flow and provide good surface contact when the water evaporates. It is not surprising that the same polymers that are useful as latex paints are also useful as latex adhesives (such as PMMA). Latex adhesives are widely employed for bonding pile to carpet backings.

Pressure-sensitive adhesives: Pressure-sensitive adhesions are actually viscous polymer melts at room temperature. The polymers must be applied at temperatures above their T_g to permit rapid flow. The adhesive is caused to flow by application of pressure. When the pressure is removed, the viscosity of the polymer is sufficient to hold and adhere to the surface. Many tapes are of this type where the back is smooth and coated with a nonpolar coating so as not to bond with the sticky surface. The two adhering surfaces can be separated, but only with some difficulty.

Hot-melt adhesives: Hot-melt adhesives are thermoplastics that form good adhesives simply by melting, followed by subsequent cooling after the plastic has filled surface voids. Nylons are frequently employed in this manner. Electric glue guns typically operate on this principle.

Reactive adhesives: Reactive adhesives are either low-molecular-weight polymers or monomers that solidify by polymerization and/or cross-linking reactions after application. Cyanoacrylates, phenolics, silicon rubbers, and epoxies are examples of this type of adhesive. Plywood is formed from impregnation of thin sheets of wood with resin, with the impregnation occurring after the resin is placed between the wooden sheets.

Thermosets: A number of thermosets have been used as adhesives. Phenolic resins were used as adhesives by Leo Baekeland in the early 1900s. Phenolic resins are still used to bind together thin sheets of wood to make plywood. Urea resins have been used since 1930 as binders for wood chips in the manufacture of particle board. Unsaturated polyester resins are used for body repair, and polyurethanes are used to bond polyester cord to rubber in tires, to bond vinyl film to particle board, and to function as industrial sealants. Epoxy resins are used in the construction of automobiles and aircraft and as a component of plastic cement.

Elastomers: Solutions of natural rubber have been used for laminating textiles for over a century. The Macintosh raincoat, invented in 1825, consisted of two sheets of cotton adhered by an inner layer of natural rubber. SBR is used as an adhesive in carpet backing and packaging. Neoprene (polychloroprene) may be blended with a terpene or phenolic resin and used as a contact adhesive for shoes and furniture.

Pressure-sensitive tape: Pressure-sensitive tape consists of a coating of a solution of a blend of natural rubber and an ester of glycerol and abietic acid (rosin) on cellophane and was developed

over half a century ago. More recently, natural rubber latex and synthetic rubber have been used in place of the natural rubber solution. The requirement for pressure-sensitive adhesives is that the elastomers have a T_g below room temperature. Today, there are many other formulations used in the production of pressure-sensitive tapes.

Contact adhesives: Contact adhesives are usually applied to both surfaces, which are then pressed together. Liquid copolymers of butadiene and acrylonitrile with carboxyl end groups are used as contact adhesives in the automotive industry.

Thermoplastics: A number of thermoplastics have been used as adhesives. Polyamides and copolymers of ethylene and vinyl acetate (EVA) are used as melt adhesives. Copolymers of methyl methacrylate and other monomers are used as adhesives in the textile industry. Poly(vinyl acetate) is often used in school glues.

Anaerobic adhesives: Anaerobic adhesives consist of mixtures of dimethacrylates and hydroperoxides (initiators) that polymerize in the absence of oxygen. They are used for anchoring bolts.

Cyanoacrylates: One of the most interesting and strongly bonded adhesives are cyanoacrylates (Super Glue, Krazy Glue). These monomers polymerize spontaneously in the presence of moist air, producing excellent adhesives. These adhesives, which have both the cyano and ester polar groups, are used for household adhesive problems as well as in surgery, mechanical assemblies, and as a *fast fix* for athletic cuts such as in boxing.

Many seemingly simple adhesive applications are actually complex. The labels on commercial dry cell batteries can contain over a dozen layers each present for a specific purpose. While price is a major consideration, ease of application is another. Thus, while many naturally derived adhesives are less expensive, synthetic materials may be chosen because of ready application and consistency of the end product.

One common use of adhesives is as the *working* ingredient of tapes. Numerous tapes are available, many with interesting stories. The ingredients vary with the intended use. Table 16.4 (Picture 16.5) contains the main ingredients of some important tapes. But, knowing the ingredients is only the start. There is much science involved. For instance, important factors involved with pressure-sensitive adhesion are a balance between allowing molecular interaction between the adhesive and adherent (often referred to as “wetting”) and the dynamic modulus of the adhesive mixture. This also involves a balance between *pull-off rate* and *wetting rate*.

TABLE 16.4 General Composition of Typical Scotch Tapes (by Weight)

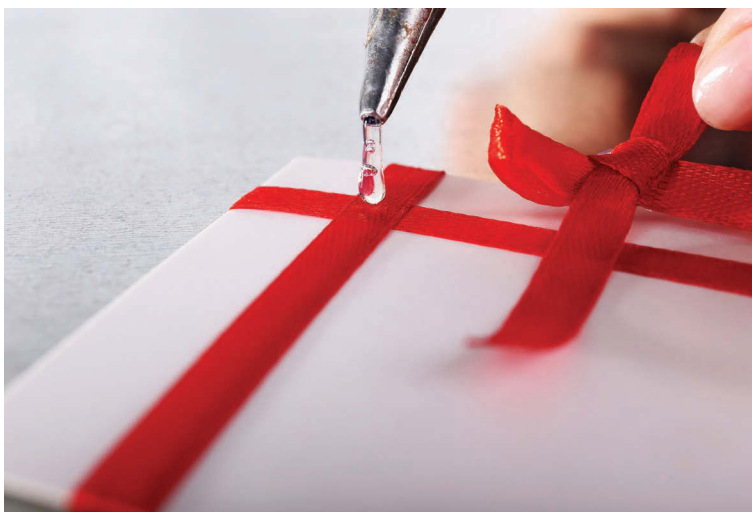
Paint masking tape
Paper backing 55%–74%
Natural rubber adhesive 26%–45%
Transparent tape
Acrylic adhesive about 36%
Polypropylene film (backing) about 64%
Post-it notes
Acrylic adhesive <0.5%
Inks and dyes <0.1%
Paper >99.5%
Vinyl electrical tape
Poly(vinyl chloride) backing 48%–54%
Polyester adipate backing 21%–27%
Hydrotreated light naphthal 4%–8%
Epoxidized soybean oil 2%–4%
Antimony trioxide (Sb_2O_3) flame control 2%–4%
Piperylene-2-methyl-2-butene polymer 2%–4%
Branched alkyl phthalate plasticizer 2%–4%
Fillers and processing aids 2%–4%



PICTURE 16.5 Different kinds of adhesive tape.

Mechanical adhesion with interlocking and diffusion factors is less important than for permanent adhesion. Pressure-sensitive adhesives, such as present in *pull-off* tabs such as Post-it Notes, contain components similar to those present in more permanent Scotch Tape, except that particles of emulsified glass polymer are added to reduce the contact area between the adhesive and the substrate. Some polymers, such as PE, might appear to be decent adhesive materials, but even in its melt, it is not exceptionally tacky. This is believed a result of the high degree of chain entanglement.

Superglue (Picture 16.6) was initially discovered in 1942 as part of the war effort in a search to make clear plastic gun sights. Superglue was discovered but it stuck to everything so was discarded. In 1951 Harry Coover and Fred Joyner, Eastman Kodak researchers, rediscovered it. It was first sold as a commercial product in 1958.

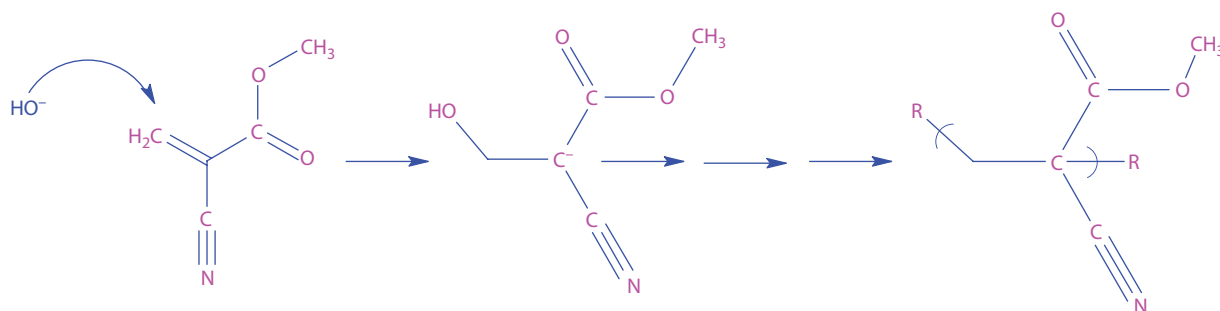


PICTURE 16.6 One of many uses for superglue. (From Shutterstock, <http://www.shutterstock.com/pic.mhtml?id=225062017&src=id>.)

It polymerizes rapidly, generally within a minute or so continuing to harden for about 24 hours. Acetone, from many finger nail polishes, can be used to soften superglue.

Superglue is based on cyanoacrylates, generally methyl-2-cyanoacrylate, ethyl-2-cyanoacrylate (sold under trade names such as Super Glue and Krazy Glue), *n*-butyl cyanoacrylate (used in veterinary glues such as Vetbond and LiquiVet and skin glues such as Indermil and Histoacryl), and octyl-2-cyanoacrylate (used as a medical glue with trade names such as LiquiBand, FloraSeal, Dermabond, SurgiSeal, and Nexaband). Cyanoacrylate glue has a low shearing strength that allows its use as a temporary adhesive where it is employed to hold an object in place and then sheared off later. It is used to assemble prototype electronics and to hold nuts and bolts in place and in building model aircraft. It is used as a forensic tool to capture fingerprints on glass and metals. The glue was first used in 1966 as a spray to retard bleeding in wounded soldiers on the battlefield until they could be properly cared for in a hospital. It has been used to stop cuts in professional fighters and to repair bones in animals. Most glues are a mixture of the cyanoacrylate but with about 10% of other materials such as poly(methyl methacrylate), hydroquinone, and small amounts of organic sulfonic acid.

Cyanoacrylates are acrylic resins that polymerize rapidly in the presence of water via attack of a nucleophile such as the hydroxide ion. This is shown in the following for methyl-2-cyanoacrylate.



(16.3)

The 3M Company has been instrumental in the discovery and improvement of many tapes. The first pressure-sensitive adhesive tape was discovered in 1925. During the depression an increasing number of items were taped together rather than discarded. Double-sided tape was used to hold together layers of metal skins to aircraft frames. But what we now know as Scotch Tape was discovered by a young 3M engineer Richard Drew in 1930. Then 3M was a small sand paper manufacturing company. Two-toned automobiles were becoming popular. Painters would mask one section while painting the second color. Parts of the first color were often ripped off when the masking material, typically simply newsprint, was removed. Drew noticed this and worked for the next 2 years developing a pressure-sensitive glue that he applied to the edges of one side of some crepe paper. While it could be easily removed by the painters, it also kept falling off. The story goes that one of the painters told a 3M representative to tell his *Scotch* bosses (an indication that 3M was cheap) to put adhesive all over the tape and not just on the edges. They did and the name stuck as did the tape. Today, 3M has hundreds of tapes sold under the *Scotch Tape* name.

Drew was then asked to develop a waterproof tape that could seal insulation panels for refrigerated railroad cars. He and fellow workers developed the clear cellophane-backed tape that is familiar today but today with a variety of different formulations.

Post-It Notes is another of the host of 3M tapes (Picture 16.7). It was discovered by Art Fry using an adhesive developed by a fellow coworker Spenser Silver with the help of Jesse Kopes in 1968. The adhesive was simply an acrylic adhesive similar to that used for many of the more permanent tape adhesives, but diluted with nonadhesive material. Silver promoted his *low-tack* reusable pressure-sensitive adhesive for 5 years within the 3M origination but with little success. Fry attended one of the sales pitches by Silver and used the formula to anchor his bookmark in his hymnbook. 3M commercialized the product in 1977, but customers would not try this new product. After giving away free samples to the residents of Boise, Idaho, they found that people liked it, so a new promotion was tried and the rest is history. By 2003, 3M came out with *super* Post-It Notes that were simply the old formula with less nonactive filler giving the Post-It Notes better adhesion.



PICTURE 16.7 Pressure sensitive adhesion paper.

16.12 CONDUCTIVE POLYMERIC MATERIALS

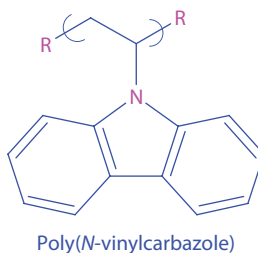
Conductance behavior is dependent on the material and what is conducted. For instance, polymeric materials are considered poor conductors of sound, heat, electricity, and applied forces in comparison to metals. Typical polymers have the ability to transfer and *mute* these factors. For instance, as force is applied, a polymer network transfers the forces between neighboring parts of the polymer chain and between neighboring chains. Because the polymer matrix is seldom as closely packed as a metal, the various polymer units are able to absorb (mute, absorption through simple translation or movement of polymer atoms and vibrational and rotational changes) as well as transfer (share) this energy. Similar explanations can be given for the relatively poor conductance of other physical forces.

Even so, polymers can be designed that compete with metals and other nonpolymer materials in the area of conductance. Following is a description of some of these materials. Covered elsewhere is described other materials that act similar to metals in the conductance of specific factors. For instance, force transference of ceramics is similar in some ways to that of metals because of a number of factors including the inability of the tightly packed ceramics to mute applied forces and their ability to directly *pass along* the results of such applied forces or stresses.

16.12.1 PHOTOCONDUCTIVE AND PHOTONIC POLYMERS

Some polymeric materials become conductive when illuminated with light. For instance, poly(*N*-vinylcarbazole), (16.4), is an insulator in the dark, but when exposed to UV radiation, it becomes conductive. Addition of electron acceptors and sensitizing dyes allows the photoconductive response to be extended into the visible and near infrared (NIR) regions. In general, such photoconductivity is dependent on the material's ability to create free charge carriers, electron holes, through absorption of light, and to *move* these carriers when a current is applied.

(16.4)



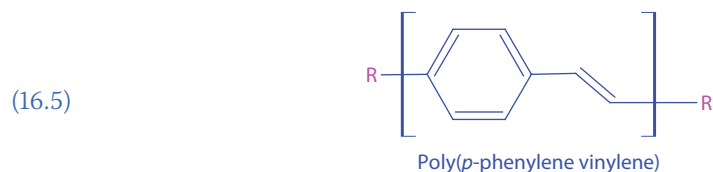
Related to this are materials whose response to applied light varies according to the intensity of the applied light. This kind of behavior is referred to as nonlinear behavior. In general, polymers with whole chain delocalization or large area delocalization where electrons are optically excited may exhibit such nonlinear optical behavior.

Photoresponsive sunglasses whose color or tint varies with the intensity of the sunlight is an example of nonlinear optical material. Some of the so-called “smart” windows are also composed of polymeric materials whose tint varies according to the incident light. Currently, much material is stored using electronic means, but optical storage is becoming commonplace with the use of CD-ROM and WORM devices. Such storage has the advantages of rapid retrieval and increased knowledge density (i.e., more information stored in a smaller space).

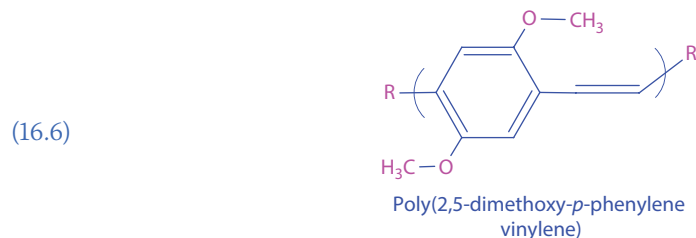
Since the discovery that doped polyacetylene becomes electrically conductive, a range of polymer-intense semiconductor devices has been studied including normal transistors and field-effect transistors, FETs, and photodiodes and light-emitting diodes. Like conductive polymers, these materials obtain their properties because of their electronic nature, specifically the presence of conjugated pi-bonding systems.

In electrochemical light-emitting cells, the semiconductive polymer can be surrounded asymmetrically with a hole-injecting material on one side and a low work function electron-injecting metal (such as magnesium, calcium, or aluminum) on the other side. The emission of light results from a radiative charge carrier recombining in the polymer as electrons from one side and holes from the other recombine.

Poly(*p*-phenylene vinylene) (PPV) (16.5) was the first reported (in 1990) polymer to exhibit electroluminescence. PPV is employed as a semiconductor layer. The PPV layer was sandwiched between a hole-injecting electrode and electron-injecting metal on the other. PPV has an energy gap of about 2.5 eV and thus produces a yellow-green luminescence. Today, other materials are available that give a variety of colors.



A number of poly(arylene vinylene) (PPV) derivatives have been prepared. Attachment of electron-donating substituents, such as dimethoxy groups (16.6), acts to stabilize the doped cationic form and thus lower the ionization potential. These polymers exhibit both solvatochromism (color change as solvent is changed) and thermochromism (color is temperature dependent).



16.12.2 ELECTRICALLY CONDUCTIVE POLYMERS

The search for flexible, noncorrosive inexpensive conductive materials has recently focused on polymeric materials. This search has increased to include, for some applications, nanosized fibrils and tubes. The conductivity for general materials is noted in Figure 16.14. As seen, most polymers are nonconductive and, in fact, are employed in the electronics industry as insulators.

The Nobel Prize in Chemistry for 2000 was given to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for the discovery and development of electrically conductive polymers. In 1975, MacDiarmid and Heeger began studying the metallic properties of inorganic poly(sulfur nitride)

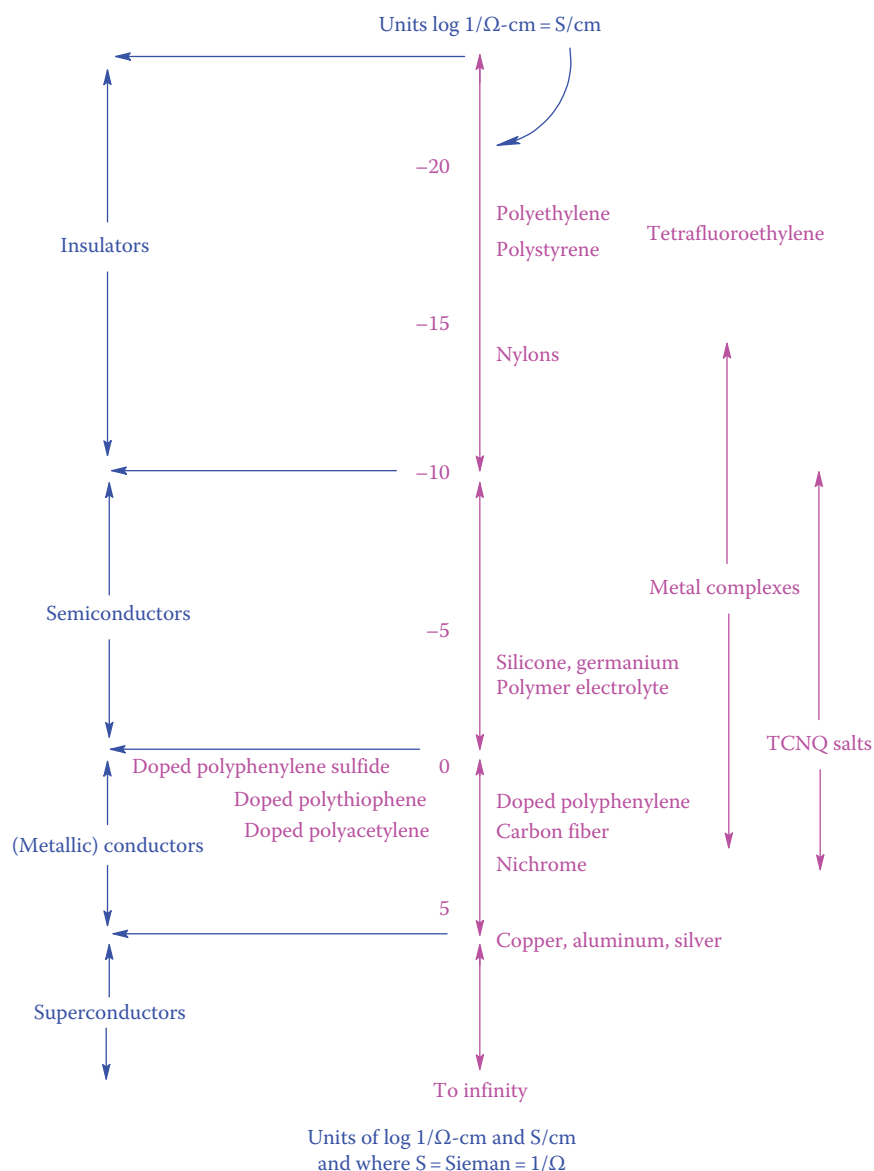


FIGURE 16.14 Electrical conductivity for various materials.

but shifted their efforts to polyacetylene after visiting with Shirakawa. While the synthesis of polyacetylene was known for years, Shirakawa and coworkers, using a Ziegler–Natta catalyst, prepared it as a silvery film in 1974. But, in spite of its metallic appearance, it was not a conductor. In 1977 using techniques MacDiarmid and Heeger developed for poly(sulfur nitride), Shirakawa, MacDiarmid, and Heeger were able to increase the conductivity of *trans*-polyacetylene samples, after doping, to a conductivity of about 10^3 S/m , or 1 S/cm . They found that oxidation with chlorine, bromine, or iodine vapor made polyacetylene film 10^9 times more conductive than the nontreated film. This treatment with a halogen was called “doping” by analogy with the doping employed with semiconductors. Other oxidizing *doping* agents have been used including arsenic pentafluoride. Reducing agents such as metallic sodium have also been successfully used. This chemical doping transforms the polyacetylene from an insulator or semiconductor to a conductor.

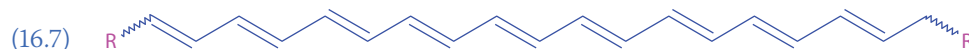
A critical structural feature for conductive polymers is the presence of conjugated double bonds. For polyacetylene, every backbone carbon is connected by a stronger localized sigma-bond. They are also connected by a network of alternating less localized and weaker pi-bonds. While conjugation is present, it is localized enough to prevent ready delocalization of the pi-bond electrons.

The dopants cause the introduction of sites of increased or deficiency of electrons. When there is a deficiency of electrons, or holes, created, electrons flow to fill this hole with the newly created hole causing other electrons to flow to fill the new hole, with this sequence repeated again and again, allowing charge to migrate within and between the polyacetylene chains.

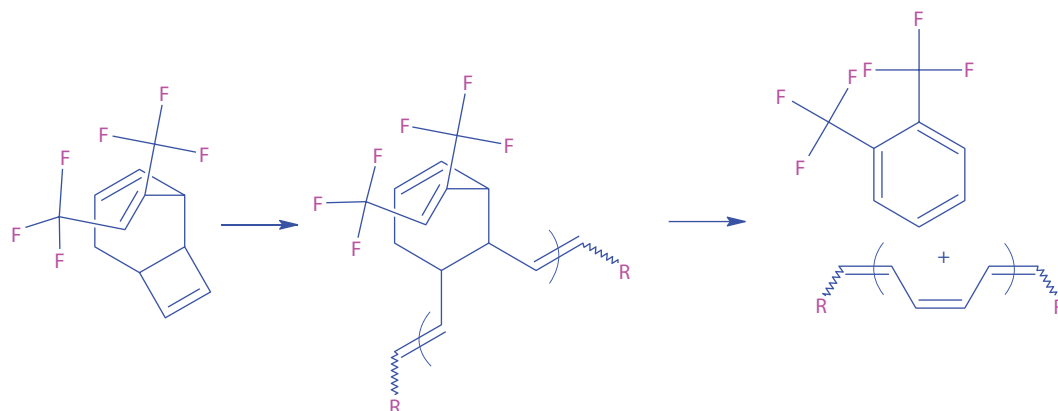
In general, the Hückel theory predicts that pi-electrons can be delocalized over an entire chain containing adjacent pi-bonds with the activation energy for delocalization, decreasing as the chain length increases. Doping provides a ready mechanism for delocalization to occur.

Ordinary polyacetylene is composed of small fibers (fibrils) that are randomly oriented. Conductivity (Sections 12.7 and 12.8) is decreased because of the contacts between the various random fibrils. Two approaches have been taken to align the polyacetylene fibrils. The first approach is to employ a liquid crystal solvent for the acetylene polymerization and to form the polymer under external perturbation. The second approach is to mechanically stretch the polyacetylene material causing the fibrils to align. The conductivity of polyacetylene is about 100 greater in the direction of the *stretch* in comparison to that perpendicular to the stretch direction. Thus, the conductivity is isotropic. By comparison, the conductivity of metals such as copper and silver is anisotropic. Of interest is the nonconductivity of diamond, which has only ordered sigma-bonds and thus no *movable* electrons and the isotropic behavior of graphite. Graphite, similar to polyacetylene, has a series of alternating pi-bonds (Equation 10.6) where the conductivity in the plane of the graphite rings is about 10^6 times that at right angles to this plane.

Polyacetylene has been produced by several methods, many utilizing the Zeigler–Natta polymerization systems. Both *cis* and *trans* isomers exist (16.7 and 16.8). The *cis*-polyacetylene is copper colored with films having a conductivity of about 10^{-8} S/m. By comparison, the *trans*-polyacetylene is silver colored with films having a much greater conductivity on the order of 10^{-3} S/m. The *cis*-isomer is changed into the thermodynamically more stable *trans* isomer by heating. As noted earlier, conductivity is greatly increased when the *trans*-polyacetylene is doped (to about 10^2 – 10^4 S/cm). Conductivity is dependent on the micro- or fine structure of the fibrils, doping agent, extent, technique, and aging of the sample.

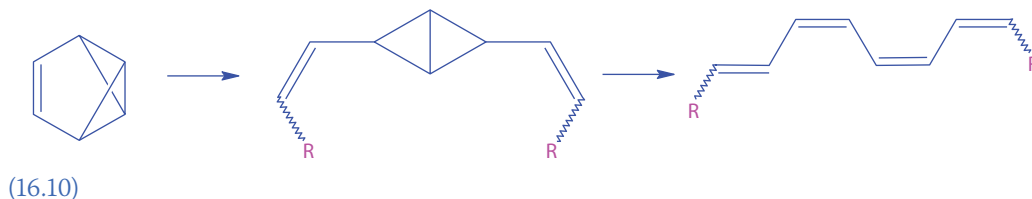


Polyacetylene was initially produced using Ziegler–Natta systems producing what have become known as Shirakawa polyacetylenes. These materials are not easily processable and are mainly fibrillar. Recently, other approaches have been taken. In the Durham route, the metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-triene gives a high-molecular-weight soluble precursor polymer that is thermally converted to polyacetylene (16.9). The precursor polymer is soluble in common organic liquids and is easily purified by reprecipitation. The end product can be aligned giving a more compact material with bulk densities on the order of 1.05 – 1.1 g/cm³.



(16.9)

Grubbs and others have used the ring-opening metathesis polymerization to produce thick films of polyacetylene and polyacetylene derivatives (16.10).



Polyacetylene has good inert atmospheric thermal stability but oxidizes easily in the presence of air. The doped samples are even more susceptible to air. Polyacetylene films have a lustrous, silvery appearance and some flexibility. Other polymers have been found to be conductive. These include poly(*p*-phenylene) prepared by the Friedel–Crafts polymerization of benzene, polythiophene and derivatives, poly(phenylene vinylene), polypyrrole, and polyaniline. The first polymers commercialized as conductive polymers were polypyrrole and polythiophene because of their greater stability to air and the ability to directly produce these polymers in a doped form. While their conductivities (often on the order of 10^4 S/m) are lower than that of polyacetylene, this is sufficient for many applications.

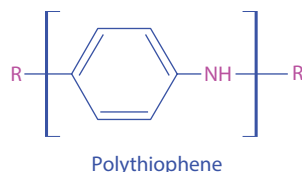
Doped polyaniline (16.11) is employed as a conductor and as an electromagnetic shielding for electronic circuits. Poly(ethylenedioxythiophene), doped with polystyrenesulfonic acid, is used as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and is also used as a hole-injecting electrode material in polymer light-emitting devices. Organic soluble substituted polythiophenes with good conductivities have been prepared. Poly(3-hexylthiophene) has a room temperature conductivity of about 100 S/cm; poly(3-methylthiophene) has a conductivity of 500 S/cm and a poly(3-alkylether)thiophene has been reported to have a conductivity of about 1000 S/cm reported. The unsubstituted polythiophene has a conductivity in the range of 50–100 S/cm. The fact that all of these substituted polythiophenes have similar conductivities indicates that there is little twisting of the backbone conjugation as alkyl substituents are added.

Polypyrrole (16.12) is being used as microwave-absorbing *stealth* screen coatings and in sensing devices. Poly(phenylene vinylidene) derivatives are being used in the production of electroluminescent displays. Polythiophene (16.13) derivatives are being used in field-effect transistors, FETs.

Following are the structures of some of the more common conjugated polymers, along with poly(acetylene), that can be made conductive through doping. As noted before, doping causes an electrical imbalance that allows electrons to flow when an electrical potential is applied. The bandgap is the energy needed to promote an electron from the valence band to the empty energy or conductive band. Metals have zero bandgaps, while insulators such as polyethylene have large bandgaps, meaning that a lot of energy is needed to promote an electron to an empty band. Semiconductors have small bandgaps where valence electrons can be moved into the conductance band through application of relatively small potential energies.



(16.13)



The optical behavior can be used to help in the understanding of these conductive materials. Pi-conjugation often occurs in the visible region so that most, if not all, of these conductive polymers are colored. Color changes are an important probe in assisting and characterizing the effects of various doping agents. Changes in the spectra allow various mechanisms to be studied. Because many of the polythiophene derivatives are organic soluble, spectral changes can be more easily studied. The electronic absorption spectra of a variety of polythiophene derivatives indicate that the band edge for conductivity begins about 2 eV.

Water-soluble derivatives of polythiophene have been made, allowing counterions bound to the polymer backbone to *self-dope* with the protons (such as lithium and sodium ions) injecting electrons into the pi-system. Thus, combinations of sodium salts and so-called proton salts (such as prepared from poly-3-(2-ethanesulfonate)thiophene) have been prepared that are both water soluble and conducting.

Another area of activity involves the synthesis of material with small bandgaps that would allow activation to occur at room temperature without doping. Polyisothianaphthene has been produced with a bandgap of about 1 eV. More recently polymers with alternating donor and acceptor units with bandgaps of about 0.5 eV and less have been developed.

While the amount of electricity that can be conducted by polymer films and *wires* is limited, on a weight basis the conductivity is comparable to that of copper. These polymeric conductors are lighter, some more flexible, and they can be *laid down* in *wires* that approach being one atom thick. They are being used as cathodes and solid electrolytes in batteries, and potential uses include in fuel cells, *smart* windows, nonlinear optical materials, light-emitting diodes, conductive coatings, sensors, electronic displays, and electromagnetic shielding.

There is a large potential for conducting polymers as corrosion inhibiting coatings. For instance, the corrosion protection ability of polyaniline is pH dependent. At lower pHs, polyaniline-coated steel corrodes about 100 more slowly than noncoated steel. By comparison, at a pH of about 7, the corrosion protection time is only twice for polyaniline-coated steel. Another area of application involves creation of solid-state rechargeable batteries and electrochromic cells. Polyheterocycles have been cycled thousands of times with retention of over 50% of the electrochromic activity for some materials after 10,000 cycles. Infrared polarizers based on polyaniline have been shown to be as good as metal wire polarizers.

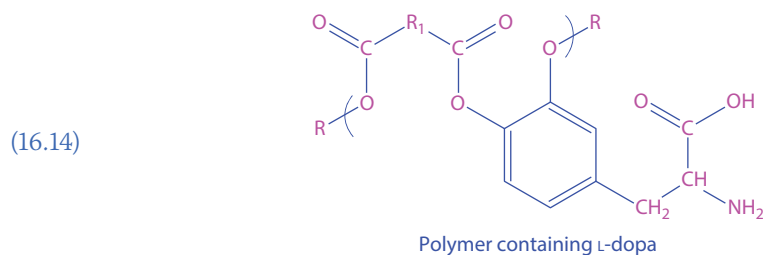
They will also find uses in nonlinear optical devices such as in optoelectronics, that is, for signal processing and optical communication. Some of the new conducting polymers offer such benefits as flexibility, high damage threshold, ultrafast response in the subpicosecond range, and good mechanical strength. Polyheterocyclic conducting polymers have shown a wide variation in color as they are electronically converted between oxidized and reduced forms. The instability of some of the polymers is being used to monitor moisture, radiation, mechanical, and chemical destruction.

16.13 DRUG DESIGN AND ACTIVITY

Most drugs are smaller molecules. But there are some drugs that are polymeric offering advantages over smaller molecules. Polymer-containing drug formulations are common. Here, the drug is contained within some polymeric matrix that assists in controlling the release either through control of drug diffusion through the chains or by erosion, degradation, or solubility of the polymer network.

Along with polymers being simply depositories of the drugs, polymers can perform active roles in drug therapy. Polymeric drugs can act in two divergent ways—as a control release agent and

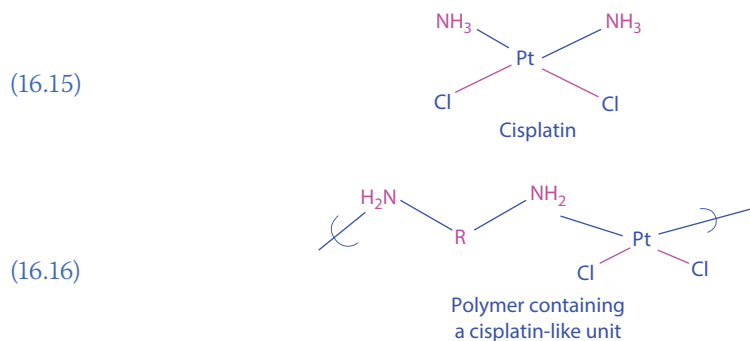
as a drug itself. The polymeric drug may act in a control release manner. Thus, a polymer that contains a known therapeutic portion can degrade, releasing this portion over some time. Thus, a polymer that contains the drug L-dopa (16.14) used to treat Parkinson's disease degrades over time releasing L-dopa over a period of time.



The polymer may act as a drug itself or the polymer drug may also act in both roles.

Following is a brief discussion of advantages of polymeric drugs that may apply to either mode of control release or as a drug itself. Because of their size, polymers with chain lengths of about 100 units and greater typically are unable to easily move through biological membranes; thus, movement is restricted. This can result in limiting negative side effects, such as damage to the kidneys, because the polymer can reside only at certain body sites. Also, this limited mobility can assist in directing the polymer drug. This also allows the use of lower and more level drug concentrations reducing renal, kidney, and bladder, damage. In some cases, multiple attachments by the same polymer chain can be beneficial. Thus, many cancer drugs act to *tie up* the DNA chains inhibiting cell replication. Here, multiple attachments to the DNA, possible for polymer drugs that contain numerous binding units within each single chain, might be beneficial in decreasing the cells effectiveness in overcoming single DNA *chemical knots* (chemical bonding together of the two DNA strands).

The polymeric nature may inhibit premature drug deactivation. Thus, cisplatin (16.15), the most widely used anticancer drug, is converted into numerous inactive, but more toxic, platinum-containing compounds before it arrives at the targeted cancer cells. Placement of the active platinum-containing platinum moiety into a polymer (16.16) decreases this tendency to hydrolyze into these unwanted cisplatin compounds because of the greater hydrophobic character of the polymeric drug.



Polymers may also evade the microorganism's defense. Recently, it was found that many cells become drug resistant after repeated treatment. Cells have groups of molecules that protect it from outside invasion. The small molecule drugs are considered *outside* invaders. Thus, drugs introduced into their environment are considered as *outside* invaders and the cell manufactures greater numbers of these *housekeepers* to rid the cell of the invaders. These *housekeeping* agents are often not very specific and remove other similar drugs that intrude their cell. These *housekeeping* proteins may not be as effective at eliminating polymer drugs.

Polymer drugs are also known to remain within human hosts longer than smaller molecules. Depending on the illness and treatment, this preferential retention may be simply due to physical retention through entanglement with biological outer-layer materials or through some specific

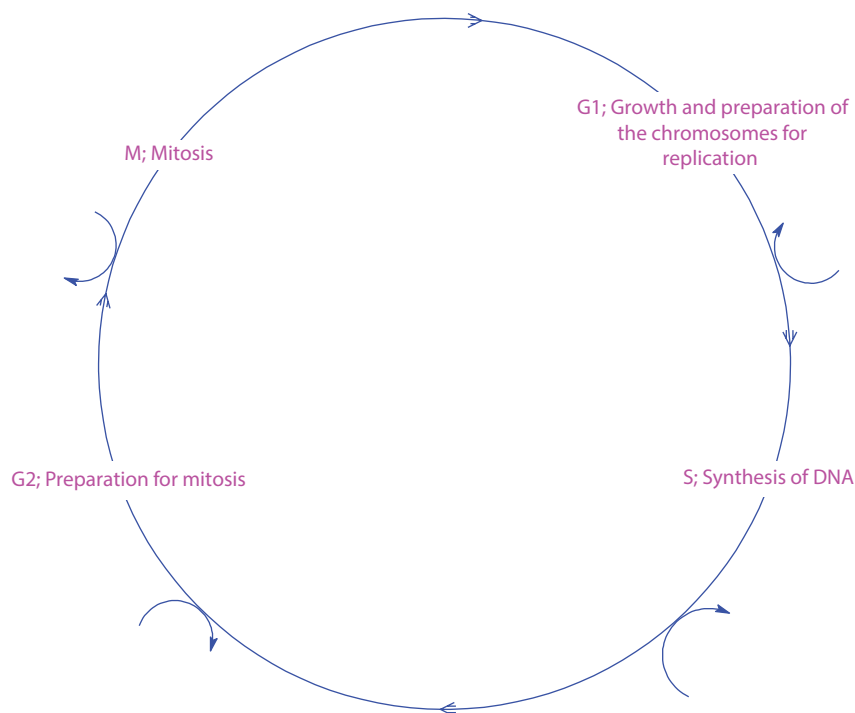


FIGURE 16.15 Cell growth cycle.

additional interaction. Tumor-associated cells are frequently hyperpermeable to plasma proteins and other macromolecules. These *leaky* vasculatures and limited lymphatic drainage, typical of tumor and missing in normal tissue, result in the accumulation of polymers. Thus, such polymers reside in the interstitial space of these cells. This results in enhanced permeability and retention of large chains.

Drug design, today, typically aims at certain specific biological activities. Thus, cancer treatments focus on controlling cell growth (Figure 16.15). Cell growth can be considered as occurring in four dependent steps. Drugs are designed to control cell growth at any one of these steps directly or indirectly. The indirect intervention of cell growth has as a target any one of many steps that influence the cell growth cycle. Essentially all chemotherapies are based on the continual growth of cancer cells compared with healthy cells generally being in some rest state.

Drugs aiming to control the same problem may target different sites. For instance, in the treatment of breast cancer, tamoxifen acts to control cell growth by blocking estrogen receptors on the cancer cell while Arimidex acts to reduce the body's estrogen production.

16.14 SYNTHETIC BIOMEDICAL POLYMERS

Synthetic polymers have been studied for some time for their use in the general field of medicine. Initial results were average. More recently, because of a better understanding of the importance of surface, avoidance of contaminants, control of molecular weight, and molecular weight distribution, the use of synthetic polymers in the biomedical sciences is increasing. Polymers are viewed as important biomedical materials for a number of reasons, some of which appear contradictory—but only because different uses require different properties. Some of the important properties are the ability to tailor-made structures, surface control, strength, flexibility, rigidity, inertness/reactivity, light weight, ease of fabrication, ability to achieve a high degree of purity, achieve water solubility/compatibility, bioerodability, and the ability of some of them to withstand long-term exposure to the human body which is a truly hostile environment. Fighting against some of the biomaterials are their limited (by volume) use; thus, researchers are often

limited to using commercial materials made for other applications, but as the use of these important materials increases, manufacturers will become more interested in tailor-making materials if for no other reason than the high cost per unit volume.

Long-term inertness without loss of strength, flexibility, or other necessary physical properties is needed for use in artificial organs, prostheses, skeletal joints, etc. Bioerodability is needed when the polymer is used as a carrier such as in controlled release of drugs, removal of unwanted materials, or where the material's purpose is short-lived such as in their use as sutures and as frames for natural growth.

Material surface is critical. While the nature of the material is important, the surface of the material is critical. The human body wants to wrap around or connect to bodies within its domain. In some cases, the desired situation is little or no buildup on the polymer. Here, surface *slickness* is needed. Siloxanes and fluorinated materials such as PTFE are generally slick materials, but other materials can be made slick through surface treatments that present to the body few voids and irregularities at the atomic level. In other cases, bodily buildup is desired and surfaces and materials that assist this growth are desired. Surface hydrophobicity/hydrophilicity, the presence/absence of ionic groups, and chemical and physical (solid or gel) surface are all important considerations as one designs a material for a specific application.

Ability to function long term is an ongoing problem. In general, polyurethanes degrade after about 1.5 years, nylons lose much of their mechanical strength after about 3 years, and polyacrylonitrile loses about 25% strength after 2 years. On the long side, PTFE loses less than 10% strength after about a year, and siloxanes retain most of their properties after 1.5 years.

Following is a brief look at some of the varied uses, real and projected, for synthetic polymers. These are intended to be illustrative only. The field of biomedical materials is rapidly growing and it is extensive.

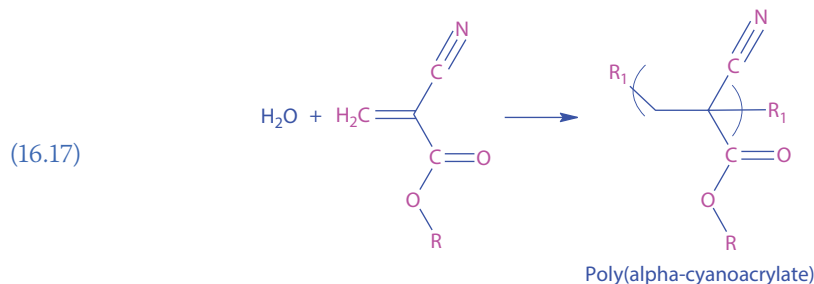
There has been a lot of effort to construct artificial hearts for human use. These hearts are largely composed of polymeric materials. With the problems associated with organ transplant, the use of artificial hearts may never be widespread. This is because of several trends. First, many biological solutions to biological problems reside with the use of biological materials to solve biological problems. With the advent of increased effectiveness of cloning and related advances, suitable biological replacements may be grown from a person's cells, thus ensuring compatibility. Second, related to the first, regeneration of essential parts of vital organs is becoming more practical. Third, because of nanotechnology and related electrical and optical advances, surgery to locate and repair imperfections is improving. Fourth, our autoimmune system is divided into two main systems—one guards against *small* invading organisms such as viruses, bacteria, and pollen. The second group acts to reject entire organisms such as the heart through rejection of foreign body tissue. Purine nucleoside phosphorylase (PNP) is a human enzyme that serves at least two major functions. First, PNP acts to degrade unleashed molecules including foreign nucleic acids. PNP is necessary to our immune system as it fights disease. Some anticancer drugs are synthetic nucleosides and nucleotides such as polypolyC, which are employed to directly attack selected cancerous tumors. PNP degrades such nucleic acid-related materials before they reach the tumor. Neutralization of PNP just prior to administration of the synthetic nucleic acid-related material would allow lower dosages to be used. Second, PNP is an integral part of the body's T-cell immunity system that rejects foreign tissue. Effort is currently underway to effectively inhibit only the PNP action, allowing the first autoimmune system to work while allowing organ transplantation without rejection. Recently, through the use of zero-gravity conditions, crystals of PNP have grown of sufficient size to allow structural determination. With this structure, efforts are underway to detect sites of activity and drugs that would allow these sites to be neutralized when needed.

Even so, synthetic polymers have been important in replacing parts of our essential organs. Thus, silicon balls are used in the construction of mechanical heart valves. Many of these fail after some time, and they are being replaced by a flap valve made from pyrolytic carbon or polyoxymethylene.

Aneurysms can be repaired through reinforcement of the artery wall with a tube of woven PTFE or polyester. Replacement of sections of the artery can be done using a tube of porous PTFE. One remaining problem is the difference in elasticity between the woven and porous materials and the arteries themselves.

Carbon fiber composites are replacing screws for bone fracture repair and joint replacements. These fiber composites are equally as strong and are chemically inert. By comparison, the metals they replace are often alloys that may contain metals that the patient may be allergic to.

Polymers are also used as sutures. Fighters and other athletics have used poly(alpha-cyanoacrylates), superglues, to quickly stop blood flow in surface cuts. Today, superglue is also used for, in place of, or along with more traditional polymeric suture threads for selected surface wounds and internal surgery and in retinal and corneal surgery. The alpha-cyanoacrylates undergo anionic polymerization in the presence of water forming polycyanoacrylates (16.17).



Siloxanes are the most extensively used synthetic biomaterial. They are used for a number of reasons including flexibility, chemical and biological inertness, low capacity to bring about blood clotting, overall low degree of biological toxicity, and good stability within biological environments.

Artificial skin had been made from a bilayer fabricated from a cross-linked mixture of bovine hide, collagen, and chondroitin B sulfate derived from shark cartilage with a thin top layer of siloxane. The siloxane layer acts as a moisture and oxygen permeable support and protects the lower layer from the *outer world*, allowing skin formation to occur in conjunction with the lower layer. Poly(amino acid) films have also been used as an *artificial* skin. Research continues in search of a skin that can be effectively used to cover extensive wounds and for burn patients.

Controlled release of drugs using polymer-intensive materials is becoming more common. The release *pack* can be attached externally such as many of the *nicotine patches* that deliver controlled amounts of nicotine transdermally. The release *pack* can also be introduced beneath the skin or within the body as is the case with many diabetes treatment assemblies.

Controlled release of drugs can be envisioned as occurring via three major routes. One approach utilizes diffusion-controlled release through membranes or matrices. Here the rate of release is controlled by the permeability of the membrane or matrix. In the second approach, the drug is captured within a matrix that undergoes degradation, usually through aqueous-assisted solubilization or degradation (including hydrolysis). Here, the rate of drug release is dependent on the breakup of the typically polymeric matrix. For the second approach, a number of polymers have been used including poly(glycolic acid) and polyanhydrides. The third approach involves simple degradation of a drug-containing polymer where the drug moiety is present as part of the polymer backbone or as side chains. Degradation of the polymer results in the release of the drug in some fashion.

Implant materials can be divided into two general categories dependent on the time requirement. Those that are present for release of a drug or to hold a broken bone in place until sufficient healing occurs are termed short-term implant materials. The second group includes materials that are to function over a longer time such as for the life of the patient. In the first case, degradation is generally required, while for the longer-term material, inertness and long-term stability are typically required. There are times when this is not true. For instance, some of the newer biomaterials act as scaffolds that promote tissue growth by providing a 3D framework with properties that encourage favorable cell growth. This material may be designed to be either short or long term. One approach to designing scaffolding material involves placing certain amino acid-containing units on the polymeric scaffold that encourage cell growth.

Another aspect related to the control of release of drugs concerns the type of structures that currently appear to be working. Not unexpectedly, because of compatibility and degradation purposes, most of the effort on the control release formulations includes polymers that have both hydrophobic and hydrophilic portions with the material necessarily containing atoms in addition

to carbon. Another concern is that the products of degradation are not toxic or do not go on to form toxic materials. It has also been found that amorphous materials appear to be better since they are more flexible and permit more ready entrance of potential degradative compounds.

Another area of activity involves the synthesis of supermolecular layers that are connected through cross-linking giving essentially one molecule thick micelles. Depending on the particular template and solvents employed, these monolayers can be designed to have almost any combination of hydrophilic and hydrophobic sites. Again, specific control of release rates, degradation times and routes, and biocompatibility or incompatibility are possible. Many of these micelle-based delivery systems are based on a poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock or on a polypeptide and poly(ethylene oxide) combination. Drug delivery has also been achieved using conducting electroactive polymers formed through controlled ionic transport of counterions (dopants) in and out of the membranes.

Hydrogels have been used that shepherd drugs through the stomach and into the more alkaline intestine. Hydrogels are cross-linked, hydrophilic polymer networks that allow the smaller drugs access to their interior and that can be designed to inflate, swell at the desired site, to deliver the drug. These hydrogels have largely been formed from materials with a poly(acrylic acid) backbone.

Along with the organic materials, a number of inorganic materials are also being considered as degradable implant material. A porous form of beta-tricalcium phosphate had been used for the repair of bone voids and related defects in the spine, pelvis, arms, and legs.

Also included in the general grouping of biomaterials are the new electronics that are being developed including nanotechnology. These electronic biomaterials will need to be encapsulated sufficiently to protect them from the body and to protect the body from hostile actions against the presence of the foreign object, or they will need to be made with a coating material that will act as an encapsulating material to the electronics device. Special care will need to be taken with respect to adhesive materials that connect the electrical device to the particular site for activity and/or interactions between the electromagnetic messages and surrounding tissue. Again, adhesive, encapsulating, and shielding materials will be largely polymeric.

A number of siloxane-containing controlled release packs have been devised and are being used. Glaucoma, motion sickness, and diabetes have been treated using drugs dispersed in a silicon matrix. This kind of pack needs to be placed near the site of intended activity for greatest effectiveness.

Elastomeric siloxanes have also been used in encapsulating drugs, in implant devices, and in maxillofacial applications to replace facial portions lost through surgery or trauma. Transcutaneous nerve stimulators are made from *conductive* siloxanes. These are employed in the treatment of chronic severe pain through application of low-level voltage to the nerves disrupting transmission of pain impulses to the brain. Siloxanes are also used in extracorporeal blood oxygenation employed in the heart–lung assist machine that is routinely used in open heart surgery. The *heart* of the apparatus is the membrane that must allow ready transport of oxygen and carbon dioxide yet retain moisture and the blood cells. The siloxane membranes can be made using a polyester or PTFE screen in an organic dispersion of silicon rubber. When dried, thin films are obtained that are used in the heart–lung assist device.

Siloxane-containing devices have been also used as contact lenses (Section 11.3), tracheostomy vents, tracheal stents, antireflux cuffs, extracorporeal dialysis, ureteral stents, tibial cups, synovial fluids, toe joints, testes penile prosthesis, gluteal pads, hip implants, pacemakers, intra-aortic balloon pumps, heart valves, eustachian tubes, wrist joints, ear frames, finger joints and in the construction of brain membranes. Almost all of the siloxane polymers are based on various polydimethylsiloxanes.

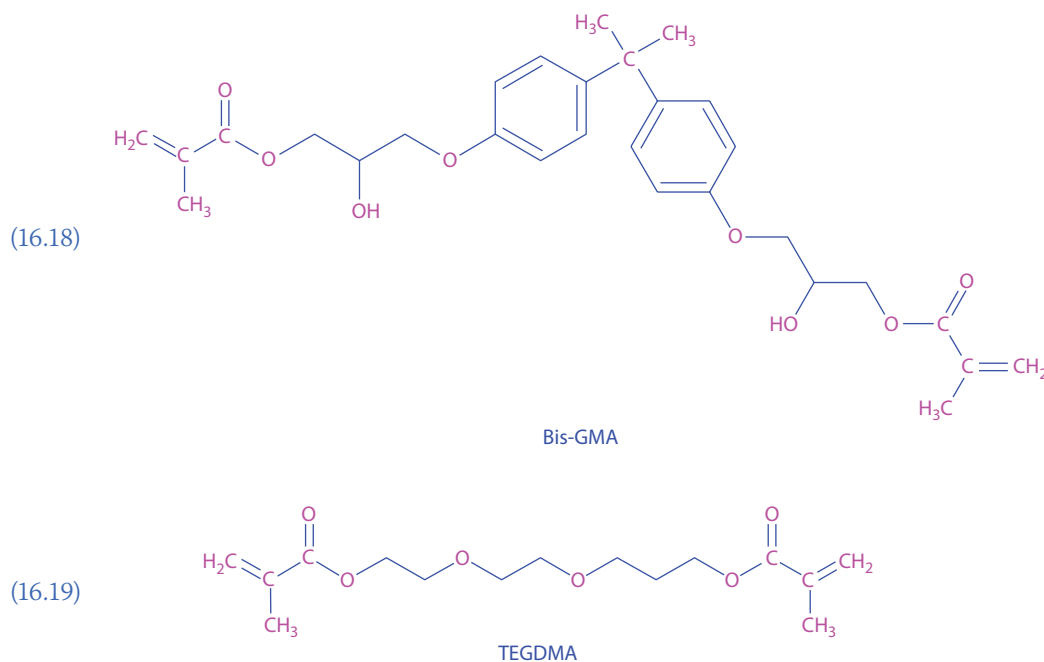
The kidney removes waste material from our blood. Because of partial or total kidney failure, many persons are on hemodialysis. The first hemodialysis units were large and by today's standards not very effective, and the semipermeable tubes, made mainly of cellophane, had very limited lifetimes. Initially, dialysis treatment was expected to be for only terminal patients, but as the life expectancy of dialysis patients increased as did the demand for dialysis, smaller, more efficient dialysis machines have emerged. At the heart of these advances is the filtering material. Today, bundles of microhollow fibers are used in the construction of hemodialysis cells. The fibers are *heparinized* to discourage blood clotting. The fibers are mainly made of polyacrylonitrile. Polycarbonate, cellulose acetate, and rayon fibers are also being used.

16.15 DENTAL MATERIALS

Polymers are used extensively in dentistry. Somewhat permanent dental materials exist in a hostile environment, the mouth, and often must resist fracture and wear under extreme forces. They must perform without fatiguing. They must also be compatible with the biological environment.

The original modern-day filling or amalgams contain various metals and alloys. More recently, composite resins often referred to as plastic or white fillings are being employed. They often consist of a mixture of powdered glass and polymer resin. They are strong, compatible, resistant, and cosmetically approach the appearance of natural teeth. Even crowns are generally metallic with a ceramic coating to approach the appearance of natural teeth.

Dental restorative composites generally consist of di- and trifunctional monomer systems that provide the cross-linking necessary to form a strong matrix once polymerized. Reinforcing fillers such as silanized quartz, ceramics, hybrid filler such as prepolymerized resins on fumed or pyrogenic silica, and ceramics act as the dispersed phase of the composite. The diluent or continuous phase is the mono- and difunctional monomer that decreases the viscosity of di- and trifunctional monomers that finally act to form the stable composite matrix. Dental sealants are similar except the filler material is either not present or in lesser concentration. Many of the restorative composites are based on modified dimethacrylates, the most common being 2,2-bis[p-(2'-2-hydroxy-3'-methacryloxypropoxy)phenyl]-propane, bis-GMA (16.18) and triethylenglycol dimethacrylate (TEGDMA) (16.19).



These two are used either separately or as a mixture. Because of the presence of the somewhat flexible ethylene oxide and related units and use of appropriate fillers, these materials give composite fillings with lower polymerization shrinkage, enhanced mechanical properties, lower solubility and water adsorption, better thermal expansion characteristics, and good biocompatibility, with aesthetic properties closely matching those of the tooth itself.

Some other fillings employ urethanedimethacrylate (1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane) in place of bis-GMA. This is an active area of research with new monomer systems being introduced in an ongoing manner.

Cavity varnishes are used to seal the exposed dentinal tubules and protect the pulp from the irritation of chemicals in the filling materials. They are generally largely natural rubber or a synthetic polymeric resin such as derived from 2-hydroxyethyl methacrylate.

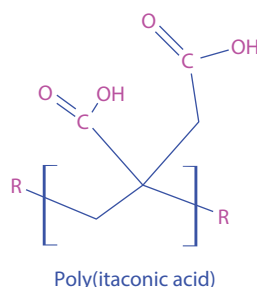
Fillings should be viewed as nonpermanent with a lifetime often of a decade. Many materials are employed in fillings including metals, alloys, amalgams, composites, and glass ionomer cements. Glass ionomer cements are a mixture of glass and an ionomer referred to as a polyalkenoic acid, which is simply an ionomer with carboxylic salt groups as the chelating moieties. The ionometric polymer chelates both the tooth and glass binding them together into the filling. Today's glass ionomer cements are especially designed for dental application. For instance, many contain releasable fluoride that prevents carious lesions with the fluoride content recharged through the use of fluoride-containing toothpaste. Newer formulations containing light-cured resins do not release fluoride as readily.

Almost all denture bases are made of methacrylic (acrylic) resins that give good fit and a natural appearance. A compression molding process is used where the monomer–polymer dough or slurry contains poly(methyl methacrylate) or poly(methyl acrylate). Often there is a change in the contour of the soft tissue, and a liner is fitted onto the denture base. Silicon reliners are often used for this purpose.

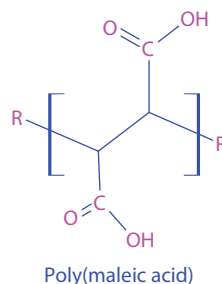
Plastic acrylic denture teeth are made by injection or transfer molding. Acrylic teeth have a higher strength than porcelain teeth and break less readily. However, they cold flow, have a greater water absorption, and have a higher wear rate than porcelain teeth.

Many of the dental polymer cements are glass ionomer combinations made from ionomer-forming polymers that contain acid groups such as poly(acrylic acid), poly(itaconic acid) (16.20), poly(maleic acid) (16.21), and poly(2-butene-1,2,3-tricarboxylic acid) (16.22). These polyalkenoate cements are set up through reaction with an aluminosilicate–fluoride glass with the polyacids hydrolyzing the glass network releasing the aluminum and calcium ions and forming a siliceous hydrogel. The acid groups chelate with the released metal cations forming a cross-linked matrix.

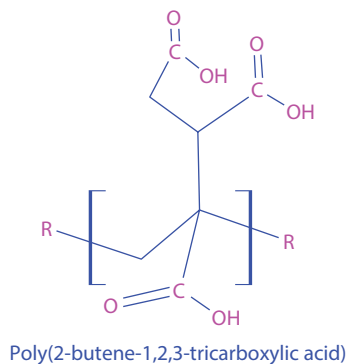
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(16.21)



(16.22)

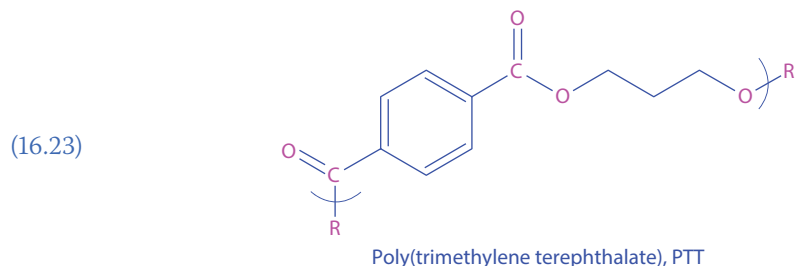


16.16 EMERGING POLYMERS

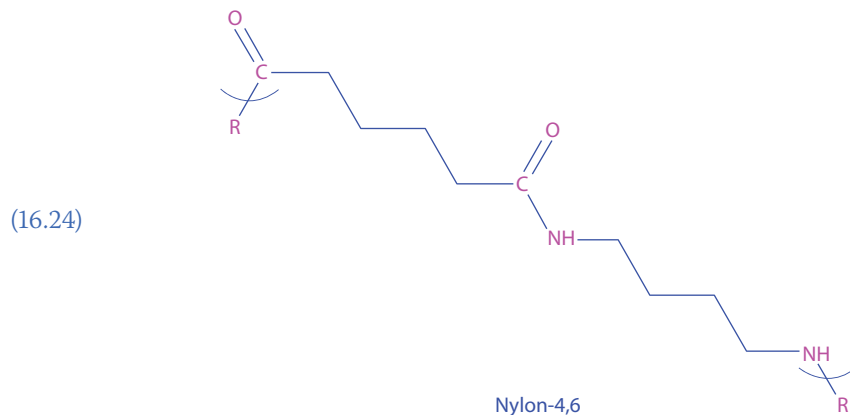
A number of small-scale polymeric materials will continue to enter the marketplace on a regular basis. These include biomaterials and electronics materials where the cost per pound is high and the poundage is low, generally well less than a hundred tons a year. These are materials that fulfill specific needs.

The number of new larger scale giant molecules that enter the marketplace will be small. It has been estimated that it takes about \$1 billion to introduce and establish a new material. It is a daunting task with no guarantee of success. In the past, new giant molecules could be introduced that offered improvements in a number of areas and thus would attract a market share in a number of application areas. Today, there are already a wide range of materials for most large-scale application areas that compete for that particular market share so that it is difficult for any material to significantly break into any market area. A new material needs a *flagship* property that a particular market needs.

DuPont and Shell have developed a new polyester, poly(trimethylene terephthalate) (PTT, 16.23), that is structurally similar to PET except that 1,3-propanediol (PDO) is used in place of ethylene glycol. The extra carbon in Sorona allows the fiber to be more easily colored giving a textile material that is softer to the touch with greater stretch. Further, it offers good wear and stain resistance for carpet use. The ready availability of the monomer PDO is a major consideration with efforts underway to create PDO from the fermentation of sugar through the use of biocatalysts for this conversion. Sorona and Lycra blends have already been successfully marketed. Sorona is also targeted for use as a resin and film.

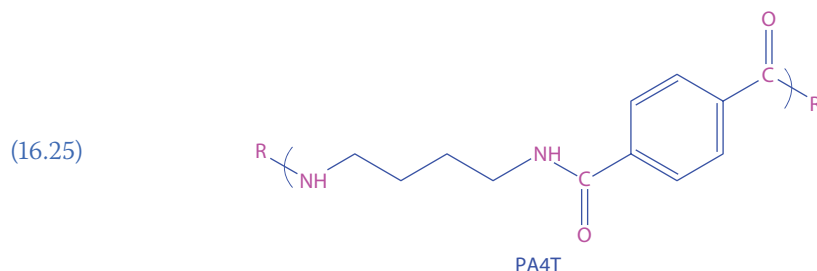


DMS introduced in 1990 nylon-4,6 called Stanyl (16.24), based on the reaction between adipic acid and 1,4-diaminobutane. Stanyl can withstand temperature of about 310°C, allowing it to create a niche between conventional nylons and high-performance materials. It was not able to break into the film market and has only now begun to be accepted for tire cord applications. About 22 million pounds of Stanyl was produced in 2001.



In 2007, DSM announced the development of PA4T nylon (16.25). It is intended to address new needs for miniaturization and the convergence of electronic devices such as cell phones and

computers. It offers good dimensional stability, compatibility with lead-free soldering, high melting point, good mechanical strength at elevated temperatures, high stiffness, and good processability. Specific applications include CPU sockets, high-temperature bobbins, notebook computer memory module connectors, and memory card connectors.



The development of PA4T nylon illustrates the use of polymers in the intermediate synthesis scale, larger than specialty chemical use and smaller than bulk chemical use. The development of polymers that fit into this category will greatly increase as special properties are needed and the price per weight is high.

In 1997, Dow introduced syndiotactic PS under the trade name Questra. The technology for the production of Questra is based on relatively new technology and science involving soluble stereoregulating catalysts that produce PS that has a fixed and repeating geometry as each new styrene monomer unit is added to the growing PS chain. Targeted areas include medical, automotive, and electronic applications.

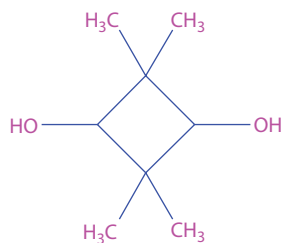
Several other produces have been developed based on the relatively new soluble stereoregulating catalysis systems. Index, an ethylene–styrene interpolmer, was introduced in 1998 and is intended to compete with block copolymers such as styrene–butadiene–styrene, flexible PVC, polyurethanes, and polyolefins. It is being used as a modifier for PS and polyethylene. Dow is also developing soundproofing and packaging foam applications for Index. Hoechst Celanese (now Ticona) developed Topas, a cycloolefin copolymer, in the 1980s and in 2000 began commercial production of it. Topas has high moisture barrier properties and is being considered for use in blister packaging for pharmaceuticals. It is also being used in resealable packages where it provides stiffness to the sealing strip. It is also being used in toner resin applications and is being blended with linear low-density and low-density polyethylene, providing stiffness and improving sealing properties.

A number of new materials are looking toward being involved in the upcoming move toward blue light CDs. For any of these to become important materials in this area, they will need to improve on the present polycarbonate-based materials.

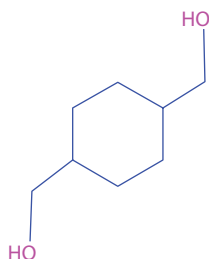
GE introduced in 2000 a new polyester carbonate based on resorcinol arylates called W-4. It is now marketed as Sollx. Sollx does not need to be painted; it offers good weather, chip, scratch, and chemical resistance and is being used as the fenders for the new Segway Human Transporter. It is also aimed at automotive uses including as body panels. Sollx is coextruded into two layers, one clear and one colored, to simulate automotive paint. It is then thermoformed and molded into the finished product.

A number of new materials have been developed because of the health fears associated with the monomer Bisphenol A, which is the comonomer for most polycarbonates. The replacement should possess similar properties to polycarbonates and also be available in large quantity and inexpensive. One material that has become available is a copolymer polyester developed by Eastman. The precise structure for this material, Tritan, is proprietary, but is believed to be based on two diols tetramethylcyclobutanediol (16.26) and 1,4-cyclohexanedimethanol (16.27). The ring systems contribute the necessary stiffness, and the methyls and methylenes supply the flexibility. These are copolymerized with dimethyl terephthalate (16.28).

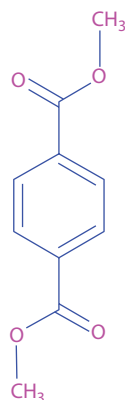
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(16.27)

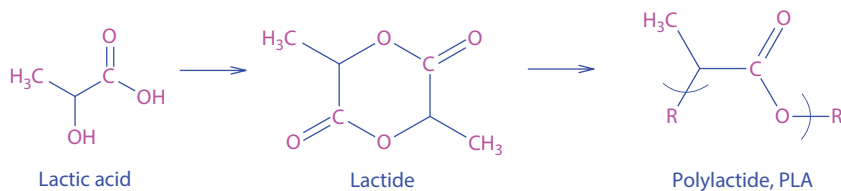


(16.28)



Several new ventures are based on using natural, renewable materials as the starting materials instead of petrochemicals. These products are known as “green” products since they are made from renewable resources and they can be composted. Along with the microbial production of PDO by Shell and DuPont to produce nylon-4,6, Cargill Dow is making PLA beginning with corn-derived dextrose. The polylactide (PLA) (16.29) is made from corn-derived dextrose that is fermented making lactic acid. The lactic acid is converted into lactide, a ring compound, that is polymerized through ring opening.

(16.29)



PLA looks and processes like PS. It has the stiffness and tensile strength of PET and offers good odor barrier and resists fats, oils, and greases. PLA is being considered for use in fibers and in packaging. As a film, PLA has good deadfold properties, that is, it has the ability to be folded and to stay folded. It is being used as a fiber for apparel and carpeting applications. It is being sold as a bridge between synthetic and natural fibers in that it processes like synthetic fibers but has the touch, comfort, and moisture management of natural fibers.

Many of the so-called new materials are actually *old materials* arranged in different settings. Following is a brief description of three of these materials. Tigris, developed by Milliken, is a PP thermoplastic composite. It is made from coextruded PP tape yarn that has a highly drawn core creating strength, additional strength for the PP yarn. The pulling encourages better alignment of the PP chains. The tape yarn is then woven into a fabric and layered and finally heated with nonyarn PP, with pressure applied forming rigid sheets that are used for panel applications or premold material. Thus, the yarn acts as the discontinuous phase with the nonoriented PP used as the continuous phase forming a PP–PP composite. In some fashion, Tigris is similar to plywood in that various layers are stacked, generally with the sheets placed at different angles to one another. The entire PP composite is strong, and it is lighter than most composites. It also has good impact resistance since the entire composite is more intimately mixed allowing more efficient transfer of impact energies. Because it is one single material, it is easy to recycle, lending it being a more environmentally friendly material. It is being used in automotive applications including at the race track. Because of its outstanding impact resistance, it is being used as the race car splitter and to reinforce other parts of the race cars. If it does fail, unlike other composite materials that often shatter leaving unwanted debris on the track, Tigris materials retain their entirety. Further, because of the layering, fractures do not propagate throughout the entire Tigris part. Other uses are in transportation as liners and floors, in water sports in the construction of small boats and watercraft, and in construction of blast resistance materials; and it is being used in the construction of playground and outdoor objects.

A second material recently introduced as Impaxx is an energy-absorbing foam developed by Dow Automotive. It reduces weight, space, and cost and improves safety. It is composed of foamed PS, so is similar to disposable coffee cups. Impaxx is a closed foam material. On impact, the closed foam cells compress and buckle absorbing energy, and when excessive impact energy is applied, the cells rupture again absorbing energy. Impaxx is used in over 2 million automobiles including the Honda Pilot, Chevy Malibu, and Ford Crown Victoria (no longer in production) as well as a number of racing cars. It is used as headliners and pillar trims, steering column and lower instrument panels, under carpet, front and rear doors, and in bumper systems. Again, it is advertised as being green friendly since it is all PS and can be readily and easily recycled.

CarbonX is made by Chapman Thermal Products and is in competition with Nomex and similar materials as a flame-resistant material. CarbonX is made by a controlled heating of polyacrylonitrile forming a fully oxidized fused polycyclic composition similar to that described in Section 10.12. The material can be heated to 500°C, 1000°C, or higher giving a material that is then stable to that temperature since material that is unstable has already been driven off. The oxidized polyacrylonitrile (OPAN) is forced through small holes resulting in the formation of tiny fiber-like materials, which are not particularly flexible. Thus, the OPAN is often woven with other fibers including steel fibers, giving the material additional strength and flexibility.

Even if some burning occurs, the OPAN fabric expands removing oxygen. CarbonX materials are replacing some of the fabrics previously made by Nomex. Nomex and CarbonX garments are made for use by firefighters, steel mill workers, military, race track drivers and other personnel, and police and include undergarments, socks, suits, head gear, shoelaces, and escape blankets. CarbonX comes in your choice of colors as long as you want black. Other colors are achieved through blending colored fibers in with the CarbonX fibers.

Safety glass is also undergoing changes. Along with the poly(vinyl butyrate), PVB, inner layers, other materials are being used including PET, EVA and ionoplast as inner layers. DuPont, Solutia, and PPG have pioneered in lots of these efforts so that the applications are not just for the automotive windshields but for many architectural uses. The U-shaped Grand Canyon Skywalk that extends 70 ft from the rim and 4000 ft above the Colorado River employs laminated glass. The balustrades have laminated bent glass of two 3/8 in. layers with a 0.06 in. PVB interlayer. The 2 in. thick glass floor has five layers of glass alternating with four layers of SentryGlas Plus. The SentryGlas Plus has an ionoplast resin composition that is five times stronger and with 100-fold rigidity compared with the traditional PVB inner layers. The walkway can support over 70 million pounds, withstand sustained winds in excess of 100 miles per hour and an 8.0 magnitude earthquake.

Head-up displays allow drivers to view important information as Global Positioning Systems on the windshield. These systems use laminated glass combinations as Wedge, which is a Butacite

PVB interlayer that converts the windshield into a transparent liquid crystal display. Wedge is also employed as outer windows for large-scale buildings with the ability to color the glass in an assortment of colors and hues.

Layered glass also contributes to savings of heat and our health. Tempered glass absorbs about 60% UV radiation, while laminated glass blocks over 90% of the UV radiation equivalent to a sun protection factor of 50.

16.17 GREEN MATERIALS

There is an increasing emphasis in so-called green materials. There are other terms often associated with the term green materials. These other terms include renewable resource materials and natural materials. The emphasis is the replacement of nongreen materials by these green materials. Each of these terms has slightly different meanings. The term *renewable materials* is generally employed for rapidly renewable materials such that are replenished within a short time such as a year. The term natural materials emphasizes materials that are derived from nature. Along with these descriptions, a green material also encompasses the energy requirements, processing procedures, and recycling ability of the material.

The American Chemical Society has described 12 principles of green chemistry. Design of reactions should incorporate assessment of all of the principles of green chemistry. These are briefly described in the following:

1. *Prevention*: It is better to prevent waste than to deal with it later. It is better to prevent an explosion than deal with its aftermath.
2. *Atom economy*: When synthesizing monomers or polymers, maximize the incorporation of reactant atoms into the product. This economy is inherent in vinyl polymerizations where the vinyl monomer is fully incorporated into the polymers. With condensation polymers, there is often a condensate that is omitted from the final polymers, but the typical condensates are water and hydrogen chloride, both essentially recovered and recycled.
3. *Less hazardous chemical syntheses*: Design reactions employing the least toxic reactants and intermediates possible taking into account that additional factors may at times override this. In such cases, moderate the toxic nature of reactants and products and be ready to deal with them safely.
4. *Design safer chemicals*: There has been an ongoing effort in the chemical industry to minimize toxicity searching for chemicals that can be employed safely on a large scale. Chemists continue to search for less toxic agents that can be employed safely. For instance, catalysts are continually being developed that are more effective (less waste/by-products), operate under milder conditions (less energy use), are less toxic, and may allow multiple synthetic steps to occur within a single synthetic sequence.
5. *Safer solvents and auxiliaries*: Along with safer solvents, there is effort to reduce or eliminate them entirely. For example, there is an effort to reduce the presence of solvents within products such as waterborne coatings.
6. *Design for energy efficiency*: There is an effort to design synthetic systems that operate under room conditions of temperature and pressure, thereby increasing energy efficiency and reducing the need for specially designed containment systems.
7. *Use of renewable feedstocks*: Today, there are numerous examples of the synthesis of polymeric materials employing either directly natural materials or more typical synthesis of monomers from renewable feedstocks, many including carbohydrates as the initial source of atoms. Related to this is the use of microbes and enzymes to synthesize monomers that already have a well-described chemical stream. Thus, the handling and recycling concerns have already been addressed for the particular monomer as well as a thorough knowledge of the properties of the monomer minimizing retooling and extensive modification of existing facilities for industrial-scale production of the associated polymers.

8. *Reduction of derivatives*: In many syntheses, use of blocking groups and other necessary tailoring of reactants should be minimized since such procedures decrease the efficiency of the procedure and generally result in eventually forming unwanted or difficulty recycled materials.
9. *Catalysts*: As already noted, there is a revolution occurring in the design and use of both natural and synthetic catalysts with the aim of promoting efficiency, energy reduction, safer conditions, higher specificity, ability to perform multiple steps, etc., under which highly specific chemical syntheses can occur. The methylaluminoxane-based catalysts are examples of stereospecific catalysts with large efficiency rates of over 25 tons of HDPE per gram of catalyst.
10. *Design for degradation*: This is better described as a design for recycling so that synthetic by-products, solvents, etc., can be easily and readily recovered.
11. *Real-time analysis for pollution prevention*: For industrial-scale syntheses, it is important to monitor the process so that the systems are running as they are intended in minimizing pollution production and other unwanted affects such as use of excess energy.
12. *Inherently safe chemistry for accident prevention*: As noted in 11, real-time monitoring of systems is important, both for small laboratory-scale and larger industrial-scale syntheses. Overheating, the presence of unwanted contaminants such as moisture or oxygen in the atmosphere, can have devastating effects on systems. Often, once a reaction begins to go *wrong*, it is the moment before dangerous conditions exist that can lead to loss of limb and life. Think about what could happen, what should happen in a reaction. If there is any question concerning safety in the design and use of chemicals, get someone that knows before you attempt to carry out the reaction. A little time lost is better than loss of life and limb.

There are generally two main approaches in developing green materials. These approaches are to create new material not traditionally available such as poly(lactic acid). The second has *biology* creating materials already being used. The second approach has the advantage of an already known technology and knowledge of the material. This second approach generally focuses on new methods to synthesize monomers. Another factor favoring the so-called “drop-in” materials is that a recycling stream already exists for the materials so that no new stream needs to be developed.

Natural materials include materials that are *naturally* found. This includes oil, coal, and natural gas. These materials are not considered green materials because they are not readily replenished. Other natural materials include silicon dioxide—intense materials such as mica that is utilized in some coatings producing clad-like coverings and diatomaceous earth that is being employed in the construction of some tires to retain tire pressure. It also includes many readily renewable materials such as cellulose, chitosan, vegetable oils, and lignin. These renewable materials are readily available in the billions of tons yearly, renewable on a regular yearly cycle, and are greatly underused materials. Carraher and others have worked with chitosan to produce anti-cancer drugs and lignin to produce materials with structural integrity as alternative industrial materials. Sperling and others have employed naturally derived oils producing various rubbers.

Here we will describe other green materials. We emphasize polymers that are commercially available and that are really derived from natural sources, not simply said to be possibly derived from natural sources. Nylon 66 was initially advertised to be derivable from various natural sources, and it is, but today, manufactured from monomers that are part of the stream of petroleum-derived feedstocks. Thus, nylon 66 is not included in this discussion as a green material, though it may become part of the green material revolution as natural, biomass-derived, sources for the reactants become available on a large scale.

The movement from a petroleum-based material to a green material is not straightforward and involves many considerations. It is a journey that we need to be careful of but a journey we need to begin. We also need to be aware that the large bulk of petroleum-based use is not as materials but rather as fuel. The drive toward biobased polymers is driven by a number of factors. These factors include financial, supply, and popular beliefs. It is also driven by scientific factors including engineered microbes and new catalytic systems. Both small startup companies and industrial giants are involved with the movement. There is the movement by larger firms to *purchase* the necessary technology through buying smaller firms with the *needed* technology. There is also

the movement for companies to join together with each entity possessing a part of the equation to move forward. Examples of partnerships are between BASF, Cargill, and Novozymes to produce biobased acrylic acid for superabsorbent materials. Coca-Cola has increased its funding of its partner Virent, the producer of the raw material allowing the production of totally biobased soda bottles. C&EN (CEN.ACS.Org, October 27, pp. 10–14, 2014) has correctly noted that “Commercializing a biobased polymer is not something that any one company can do on its own. It requires sustained, parallel progress on several fronts including technology development, end-product verification, market demand, and robust business acumen.”

There are some concerns that need to be considered in the production of products from green materials. A major emphasis in the production of materials from synthetic polymers is that they are inert, not offering unwanted biological activity and decomposition. The idea that green materials should be naturally recyclable runs against this concept. Another concern involves the actual net energy and resources necessary to produce the monomer–polymer product. An analysis needs to be made concerning the various components such as energy and resource (including water) requirements before a green material is accepted as a replacement. Another consideration is the ready availability of the particular green material. A material may be green, but if it is not readily available or can be seen as readily available in sufficient amount, then it may not be a strong candidate to be employed on a large-scale commercial basis. Also, the behavior or properties of the green material should at least approach the materials that may be replaced.

As our bioengineering revolution matures, it should be possible to employ various biomasses as resources that can be converted into classical monomers such as ethylene, propylene, styrene, and terephthalic acid from reactions caused by genetically designed microbes. In fact, it may be possible for combinations of microbes to produce finished polymers that may have better tacticity and chain orientation producing polymers with superior physical properties.

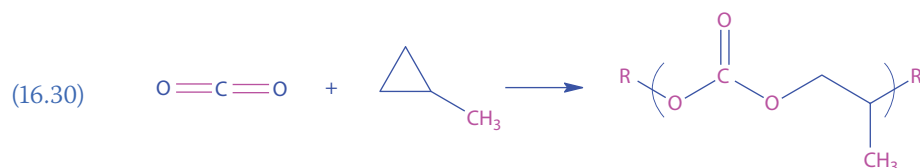
The latest major emphasis on a major green material is PLA discussed in the previous section. The use of rayon and other materials derived from cellulose has also been discussed.

There are many vegetable oils that are currently available on an industrial scale. These include palm, soybean, cotton seed, castor, and rapeseed oils. While these have been employed in the production of many commercial materials such as coatings, pharmaceuticals, plasticizers, and building materials, the particular fatty acids are being used as polymeric materials. Three of the five most common fatty acid substituents, oleic acid, linoleic acid, and linolenic acid, are unsaturated with these sites of unsaturation available for cross-linking. These are pictured in Figure 16.16. These fatty acids have been directly polymerized through the double bond(s).

Castor oil produces ricinoleic acid on its hydrolysis. Ricinoleic acid has a single olefinic site as well as both an acid and an alcohol group (Figure 16.16). Thus, it can be polymerized by reaction through its double bond or by condensation, as shown by Carraher and workers, with a Lewis acid. Polyesters have also been produced through the formation of the lactone followed by ring-opening polymerization (ROP).

One area of activity involves the production of polyurethanes employing fatty acids as well as the oils themselves. Often the oil is functionalized with hydroxyl groups through reaction at the unsaturated sites. The reaction is analogous to that employed to produce a number of soft–hard block polyurethanes.

Carbon dioxide is readily available and renewable. It is employed in the production of polycarbonates but can also be utilized in the production of various polymers through reaction with different heterocycles such as aziridines, episulfides, and epoxides. The production of PP carbonate (16.30) has been known for about 40 years, but it has yet to be commercially produced.



There are a number of biodegradable polyesters including poly(glycolic acid) (PGA; 16.29), poly(lactic acid) (PLA), poly-3-hydroxybutyrate (PHB; 16.30), and polycaprolactone (PCL; 16.31). PGA, PLA, and PCL are synthesized from the acid-catalyzed ROP of the internal ester. PHB is

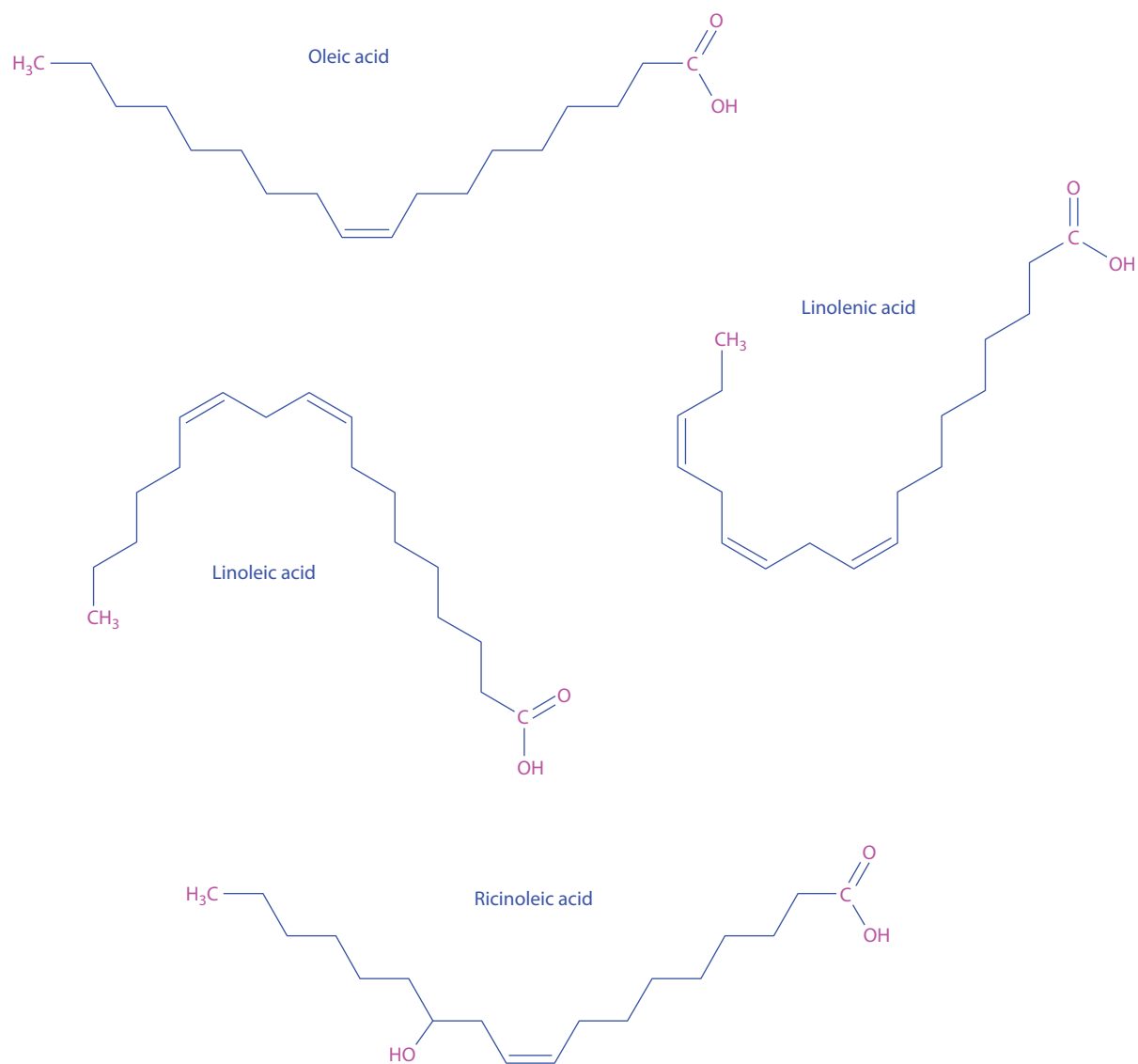
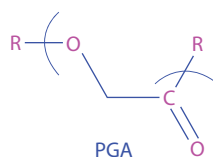


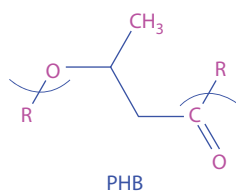
FIGURE 16.16 Vegetable oil-derived fatty acids.

made from microorganisms such as *Alcaligenes eutrophus* and *Bacillus megaterium* from natural materials such as starch or glucose. PHB has properties similar to those of PP. It is stiff and brittle, has a relatively high melting point of about 180°C, and unlike PP is biodegradable. However, PP is much tougher. PHB is commercially available from Metabolix. It is an example of a larger group-
ing of synthetic polyesters called PHAs.

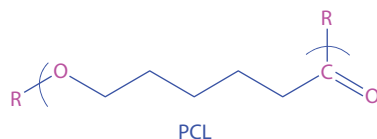
(16.31)



(16.32)



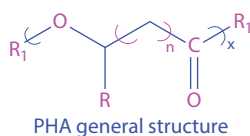
(16.33)



This theme of employing bioengineers, namely, bacteria, to produce polymers is illustrated in the synthesis of a group of over 150 linear polyesters called polyhydroxyalkanoates (PHAs; 16.32). Over 150 species of both gram-negative and gram-positive bacteria have been found to produce a variety of PHAs. For instance, *A. eutrophus* is placed in a medium that allows it to rapidly reproduce. After a sufficient population is obtained, the conditions are changed resulting in the production of a range of PHBs with general structures as shown (16.32). *A. eutrophus* typically produces so-called short-chain PHAs where $n = 3-5$. By comparison, *Pseudomonas oleovorans* produces longer chained PHAs where $n = 6-14$.

The main selling point for PHA resins, sold under the trade name of Mirel, has been its biodegradability. Tella, a joint venture between Metabolix and Archer Daniels Midland, has built a 50,000 ton-per-year plant in Clinton, IA, near its feedstock corn sugars. Its tear and puncture resistance is similar to that of linear low-density PE.

(16.34)

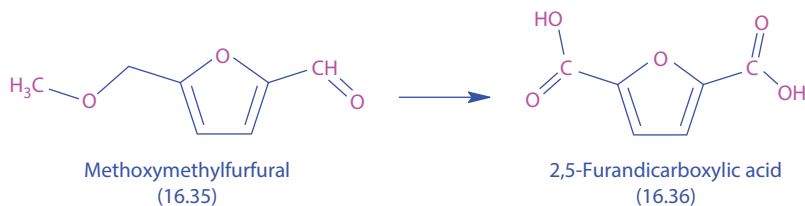


PHB has $n = 1$ and $R = \text{methyl}$. PHB is biocompatible and is a metabolite normally present in blood. Thus, a wide range of biomaterial uses can be envisioned for it. The copolymer of PHB and PHV (where $R = \text{ethyl}$ and $n = 1$), poly(−3-hydroxybutyrate-*co*-3-hydroxyvalerate), is considered as a packaging material. Compared to PHB the copolymer is tougher, less rigid, and easier to process.

The general properties can be predicted knowing the values of R and n . As expected, the smaller the value of n , the stiffer the backbone, and the larger the R , the greater the flexibility because the ability of the chains to coalesce is less because of greater steric requirements. Values of X generally range from 100 to over 30,000.

PHAs are viewed by microorganisms as an attainable energy source so are biodegradable. The end products under aerobic conditions are carbon dioxide and water, while methane is produced in anaerobic environments. They can also degrade under simple physical conditions with the ester moiety attacked by water, acid, and base. Mirel breaks down in soil and marine environments, so it is a prime contender as bags in areas where plastic shopping bags are under regulatory threat or where waste is composed.

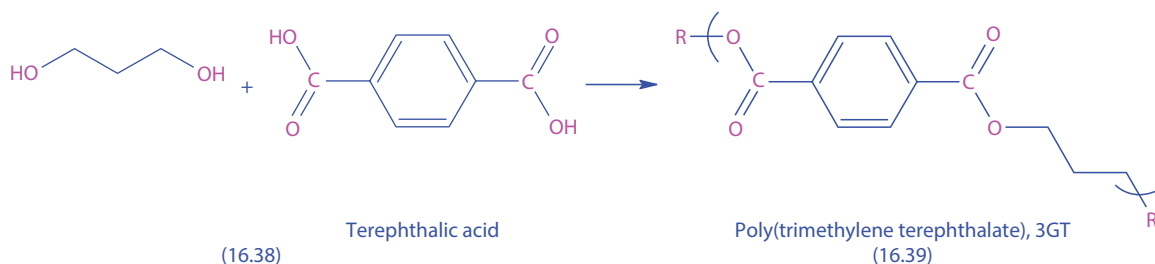
Avantium is producing another biodegradable polymer from methoxymethylfurfural (16.35) and other hydroxymethylfurfural (HMF) ethers from glucose and fructose. They have another catalyst that converts the ethers into furandicarboxylic acid (FDCA; 2,5-furandicarboxylic acid, 16.36) that is reacted with glycol to produce polyethylene furanoate (PEF) polyester. PEF is forecast to be a possible competitor to PET in bottle and container applications. The oxygen barrier of PEF is six times greater than PET so will be able to hold the *fizz* in soda bottles longer. It also has good high-temperature stability so is looking at application in the hot-filled container market.



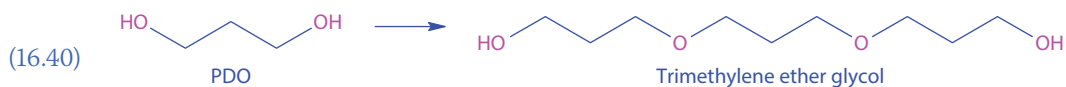
Both nylon-9 and nylon-11 (16.37) can be synthesized from biomaterials. Nylon-11 is commercially available and synthesized from monomers produced from vegetable oils, particularly from the castor plant.



DuPont has developed several polymers derived from monomers created from renewable resources. Sorona, 3GT, is a thermoplastic polyester fiber based on the reaction between PDO (16.38), where the PDO is created from corn and terephthalic acid creating the poly(trimethylene terephthalate), 3GT (16.39). The corn is converted to sugar and the sugar fermented in the presence of certain bacteria that convert it to PDO.



Hytrel is a thermoplastic polyester and elastomer, TPC-ET, containing 20%–60% polyol, Cerenol, derived from corn. Cerenol is synthesized from the self-reaction of PDO with itself and includes a variety of polyols of different chain lengths with molecular weights from about 500 to 2000. The following (16.38) shows the formation of a trimethylene ether glycol from reaction with three molecules of PDO. This diol is then reacted in the usual fashion giving polyesters with the expected hard (terephthalic derived moiety) and soft (polyol derived moiety) segments.



There are a variety of blends that are using various biomaterials including celluloses and proteins that are also being investigated and employed.

There are three major avenues for the synthesis of rubber. These are extraction of rubber latex from the latex-bearing trees, synthesis of rubber monomers from petroleum, and the biobased synthesis of monomers employed to synthesize rubber. The three major monomers employed in the synthesis of a range of rubber products are isoprene, isobutene, and butadiene. Glucose is a six-carbon compound that has already been converted via fermentation employing microbes into these three monomers. Interestingly, part of the drive toward natural derivation of such monomers is the change from multicarbon feedstocks, namely, petroleum oils, to natural gas, a single carbon material. Also in competition will be the use of sugar for other uses including food. Even so, as we become more efficient in converting our plant wastes into glucose, the ability to convert glucose into other feedstocks cost-effectively increases.

Investia, a DuPont spinoff, is producing Lycra brand spandex derived from 70% dextran. This was accomplished using biobased 1,4-butanediol, BDO, from BASF who in turn manufactured the BDO with technology licensed from Genomatica, thus the reoccurring theme of partnerships.

In 2004, the Department of Energy (DOE) identified companies staged to produce prepolymer intermediates. Many of these becoming realized for 2012–2020 (Figure 16.17). There are others listed by the DOE that are possible for the near future, next 10–15 years.

Recently, tire companies have extracted silica from rice. Rice hulls are burned and the ash contains about 90% silicon dioxide. Because of the large quantity of rice grown as a food, on the order of 700 million tons annually, the amount of silica that can be derived is on the order of 25 million tons,

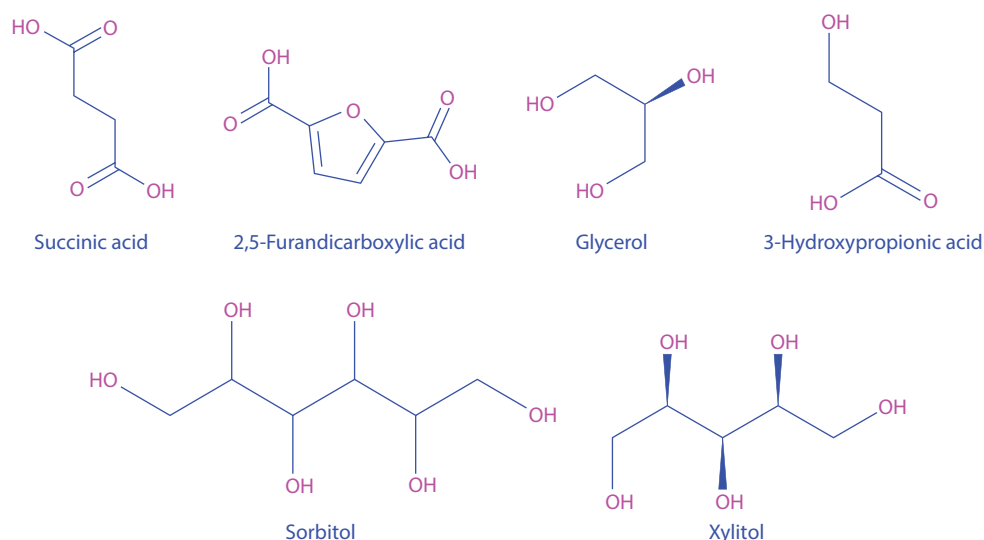


FIGURE 16.17 Biobased intermediates from natural materials.

more than 30 times the amount needed for tires. Thus, it is an almost untapped source of silica that does not take away from food production and assists in removal of currently unwanted waste.

Thus, there exist a number of possible green polymeric materials that are available for commercialization. More will be developed.

SUMMARY

1. The processing of polymeric materials is well advanced in science, engineering, and technology and continues to advance. The properties of the end product are dependent on the chemical structure, processing, and physical structure. The properties depend on the mesostructure of the particular polymer.
2. Fibers are processed using mainly one of three processes—melt spinning where the polymer is melted and forced through spinnerets, dry spinning where the dissolved polymer is forced through a spinneret and the solvent removed, and wet spinning where the dissolved polymer is forced through a spinneret into a nonsolvent bath. Fibers are usually stretched as they are formed allowing the chains to further align giving added strength in the direction of the pull.
3. Elastomers are processed using four basic steps—mastication, incorporation or compounding, shaping, and vulcanization.
4. Film and sheets are made from precipitation and/or regeneration from a polymer solution or melt. Calendering is also used where the polymer is passed between a series of counterrotating rollers.
5. Unicellular (closed cell, discrete unit cells) and multicellular (open cells, interconnecting cells) foams are made through the chemical and physical introduction of gases.
6. A wide variety of composites are made. Composites have two phases, the continuous or matrix phase that surrounds the discontinuous or dispersed phase, usually a fiber material. Composites are strong with many uses.
7. Molding employs a mobile prepolymer that may be thermoset or using a thermoplastic polymer. The polymer can be injection molded (often for solid objects), blow molded (for hollow objects such as bottles), rotational molded, compression molded, transfer molded, and thermoformed. Casting is closely related to molding except pressure is typically not used.
8. In extrusion, a fluid material is forced through a shaping device. The melts are extruded as pipes, sheets, films, or molds.

9. Coatings and paints are used for decoration and protection. There are many different kinds of coatings with the majority being latex based where the polymer is present in a suspension that forms a film when the water evaporates. Industrially, coatings are applied using roll coating, blade coating, and curtain coating processes.
10. The difference between coatings and adhesives is that coatings must adhere on only a single surface, but adhesives must bind together two surfaces. There is a wide variety of adhesives that make use of various polymer properties. Adhesion can occur through physical locking together, through chemical (primary and secondary bond formation) joining, or through simply highly viscous material holding together the assembly.
11. Polymers are major materials in the nanotechnology revolution such as conductive (photo and electronic) products. Delocalization of electrons throughout a polymer chain or matrix is important for electronic conductance. This is often accomplished through doping that encourages flow of electrons.
12. Polymers are also major materials in biomedical areas as materials and in the delivery of drugs.
13. For new polymeric materials to enter the marketplace, many things must be in place including a *flagship* property that meets a particular market need, ready availability, and money. It takes about \$1 billion to introduce and establish a new polymer into the bulk polymer marketplace.
14. There is an increased awareness and much activity involving the development of green materials and green practices. This awareness involves public awareness, increased petroleum cost, recognition that the petroleum reserves are limited, and increased ability to employ microorganisms to synthesize needed materials. This awareness also involves realizing that we need to take care of our environment, with us being responsible caretakers of the world in which we reside.

GLOSSARY

Abaca: Hemp-like fiber.

Acrilan: Polyacrylonitrile-based fibers.

Acrylic fibers: Polyacrylonitrile-based fibers.

Adhesive: Material that binds, holding together two surfaces.

Biaxial orientation: Process where a material, normally a film, is stretched in two directions at right angles to each other.

Buna-N: Acrylonitrile–butadiene copolymer.

Calender: Machine for making polymeric sheets using counterrotating rolls.

Casting: Production of film by evaporation of a polymeric solution.

Cellophane: Regenerated cellulosic film.

Charge: Amount of polymer used in each molding or processing cycle.

Coextruded film: Film produced by the simultaneous extrusion of two or more polymers.

Dacron: Trade name for PET fiber.

Draw: Depth of mold cavity.

Drying oils: Liquids employed in coatings that will be cured, cross-linked.

Dry spinning: Process for obtaining fiber by forcing a solution of a polymer through holes in a spinneret and evaporating the solvent from the extruded material (extrudate).

Elastomer: Rubber.

Electrodeposition: Use of an electric charge to deposit polymer film or aqueous dispersions onto a metal substrate.

Engineering material: Material that can be machined, cut, drilled, sawed, etc.; must have sufficient dimensional stability to allow these actions to occur.

Extrusion: Fabrication process in which a heat-softened polymer is continually forced by a screw through a die.

Fibrillation: Process for producing fiber by heating and pulling twisted film strips.

Filament: Continuous thread.

Filament winding: Process in which filament is dipped in a prepolymer, wound on a mandrel, and cured.

Gate: Thin sections of runner at the entrance of a mold cavity.

Green materials: Includes materials that do not have a negative impact on the environment; biomass-derived materials.

Hemp: Fiber from plants of the nettle family.

Hevea rubber: Natural rubber; *Hevea brasiliensis*.

Hycar: Trade name for Buna-N elastomer.

Jute: Plant fiber used for making burlap.

Kodel: Trade name for PET fiber.

Lacquers: Polymer solutions to which pigments have been added.

Lamination: Plying up of sheets.

Latex: Stable dispersion of a polymer in water.

Mechanical goods: Generally industrial rubber products like belts.

Melt spinning: Process of obtaining fibers by forcing molten polymer through holes in a spinneret and cooling the filaments.

Molding powder or compound: Premix of resin and other additives used as a molding resin.

Multicellular: Open celled.

Neoprene: Trade name for polychloroprene.

Nonwoven textiles: Sheet produced by binding fibers with a heated thermoplastic.

Oil paints: Suspension of pigments in a drying oil.

Oil varnish: Polymer dissolved in a drying oil.

Parison: Short plastic tube that is heated and expanded by air in the blow-molding process.

Perlon: Trade name for some polyurethane fibers.

Photoconductive: Material that is conductive when exposed to light.

Photoresponsive: Material whose properties change when exposed to light.

Pigment: Coloring material; colorant.

Polyacetylene: Polymer whose conductivity increases when doped to be a conductor.

Printing ink: Highly pigmented coatings used in printing.

Pultrusion: Process in which filaments are dipped in a prepolymer, passed through a die, and cured.

Rotational molding: Polymer added to a warm, rotating mold; centrifugal force distributes the polymer evenly.

Rovings: Multiple untwisted strands of filaments.

Runner: Channel between the sprue and the mold cavity.

Screen pack: Metal screen that prevents foreign material from reaching the die in an extruder.

Specific strength: Strength based on mass rather than area.

Spinneret: Metal plate between the nozzle and runner.

Sprue: Tapered orifice between nozzle and runner. Term also used to apply to plastic material in the sprue.

Structural foams: Polymeric foamed article with a dense surface.

Styrofoam: Trade name for foamed polystyrene.

Technology: Applied science.

Tenacity: Fiber strength.

Thermoforming: Shaping of a hot thermoplastic sheet.

Transfer molding: Process in which a preheated briquette or preform is forced through an orifice into a heated mold cavity.

Vehicle: Liquid in a coating.

Wet spinning: Obtaining fibers by precipitation of polymeric solutions.

EXERCISES

1. Which is more important: (a) polymer science or (b) polymer technology?
2. Name three important natural fibers.
3. Name an important regenerated fiber.

4. Why is secondary cellulose acetate more widely used than the tertiary cellulose acetate?
5. What is the difference between rayon and cellophane?
6. Name three important synthetic fibers.
7. Name an elastomer produced by (a) cationic, (b) anionic, (c) free radical, and (d) step-reaction polymerization techniques.
8. How is LDPE film produced?
9. Why is there a trend toward the use of less solvent in polymeric coatings?
10. What is meant by trade sales?
11. What are the general steps needed before a new drug comes to market?
12. How would you produce a unicellular foam?
13. Which foam is preferable for upholstery: (a) unicellular or (b) multicellular?
14. Why do non-flame-retardant foams burn readily?
15. Why has reinforced plastic been used as an automobile body?
16. Why is graphite-reinforced epoxy resin a good candidate for parts in future automobiles?
17. Why are molded thermoplastics used more than molded thermosets?
18. Which of the following might you expect would increase their conductivity when doped: (a) PS, (b) PPO, (c) nylon 66, or (d) aramids?
19. Why are structural foams used for complex furniture?
20. What are some of the advantages of a blow-molded PET bottle?
21. Why would an article be thermoformed instead of molded?
22. What is the limit to the length of an extrudate such as PVC pipe?
23. Name three popular laminates.
24. Why are the terms painting and coating often used interchangeably?
25. Why have latex waterborne coatings been popular with the general public?
26. Differentiate oil paints, oil varnishes, latexes, enamels, and lacquers from each other.
27. Briefly discuss the popular mechanisms related to adhesion and the general types of adhesives.
28. Why is there an industrial move toward the so-called green material?
29. Why is there such a broad definition as to what green materials mean?
30. Name three polymeric green materials.
31. What does the term *drop-in* materials mean?

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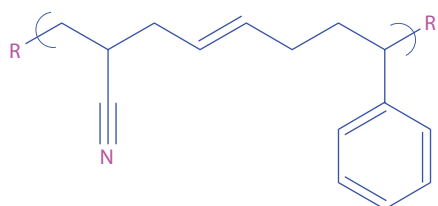


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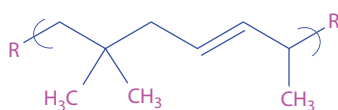
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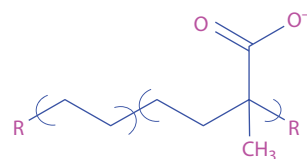
Appendix A: Structures of Common Polymers



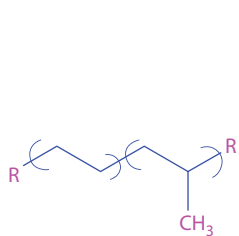
Acrylonitrile-butadiene-styrene (ABS)



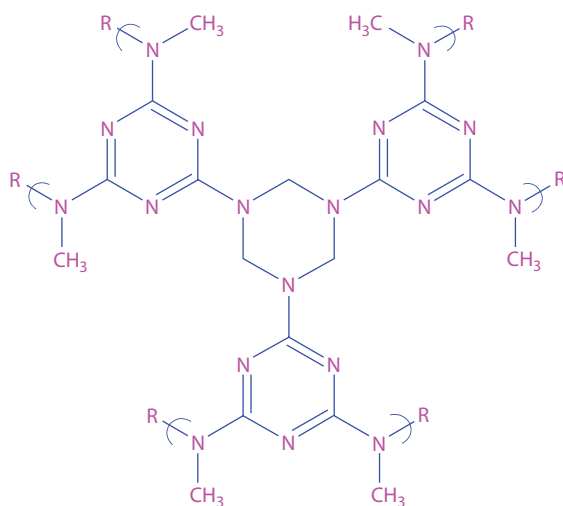
Butyl rubber



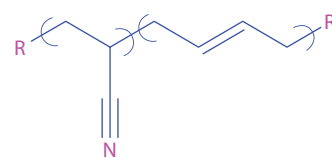
Ethylene-methacrylic acid copolymer (ionomer)



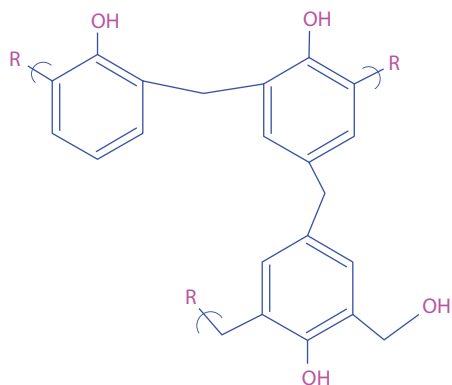
Ethylene-propylene elastomer



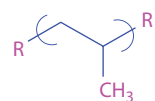
Melamine-formaldehyde resin (MF)



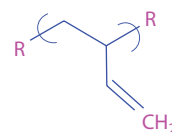
Nitrile rubber (NRB)



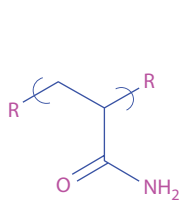
Phenol-formaldehyde resin (PF)



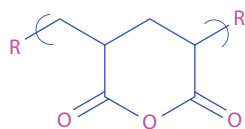
Polyacetaldehyde



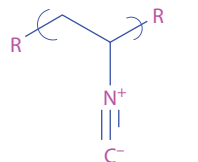
Polyacrolein



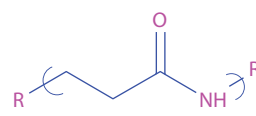
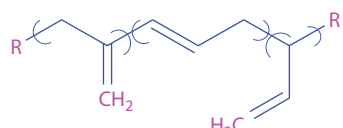
Polyacrylamide



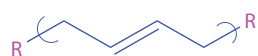
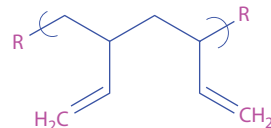
Poly(acrylic anhydride)



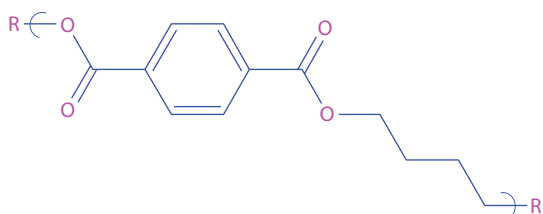
Polyacrylonitrile

Poly(β-alanine);
nylon-3

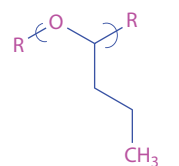
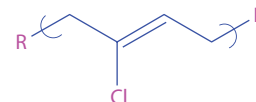
Polyallene

Polybutadiene, butadiene
rubber (BR)

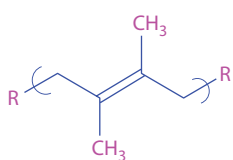
1,2-Polybutadiene



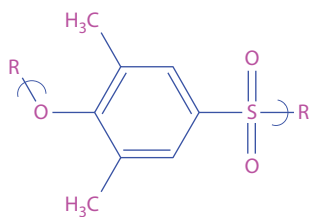
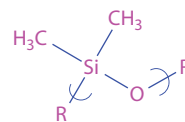
Poly(butylene terephthalate) (PBT)

Poly(*n*-butyraldehyde)

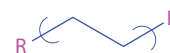
Polychloroprene



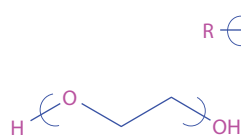
Poly(2,3-dimethylbutadiene)

Poly(3,5-dimethyl-1,
4-phenylene sulfonate)

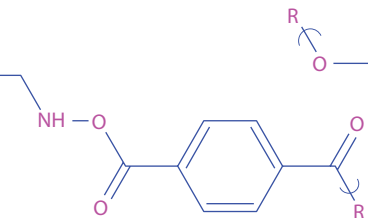
Polydimethylsiloxane



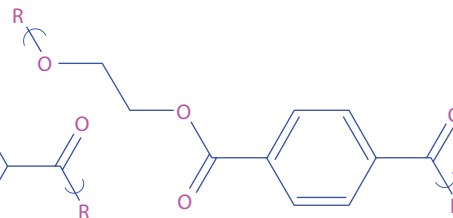
Polyethylene (PE)



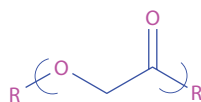
Poly(ethylene glycol) (PEG)



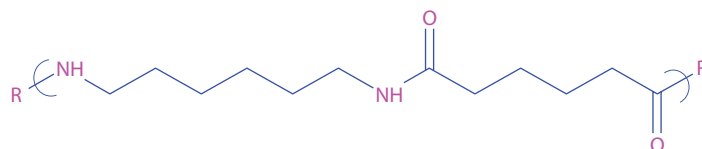
Poly(ethylene terephthalamide)



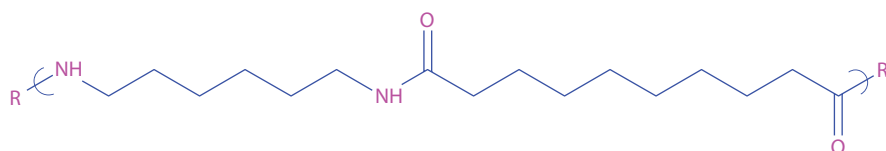
Poly(ethylene terephthalate)



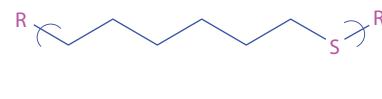
Poly(glycolic ester)



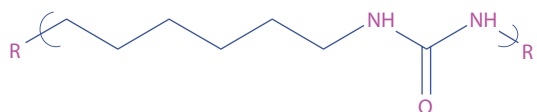
Poly(hexamethylene adipamide) (nylon 66)



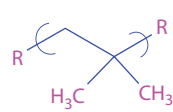
Poly(hexamethylene sebacamide) (nylon-610)



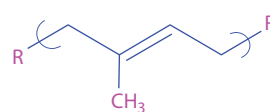
Poly(hexamethylene thioether)



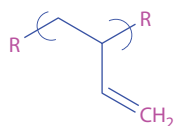
Poly(hexamethylene urea)



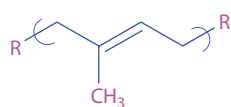
Polyisobutylene (PIB)



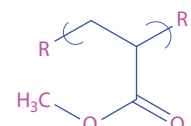
Polyisoprene



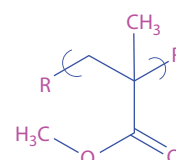
Poly-3,4-isoprene



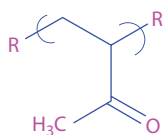
Poly-trans-1,4-isoprene



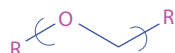
Poly(methyl acrylate)



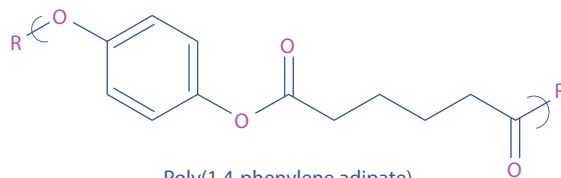
Poly(methyl methacrylate)



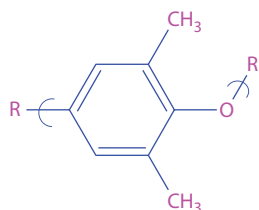
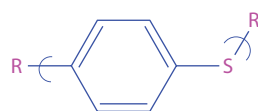
Poly(methyl vinyl ketone)



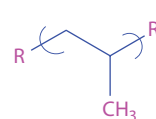
Polyoxymethylene, polyacetal



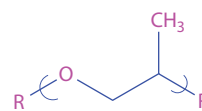
Poly(1,4-phenylene adipate)

Poly(phenylene oxide) (PPO)
Poly(2,6-dimethyl-*p*-phenylene ether)

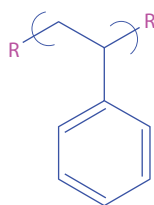
Poly(phenylene sulfide) (PPS)



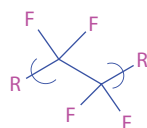
Polypropylene (PP)



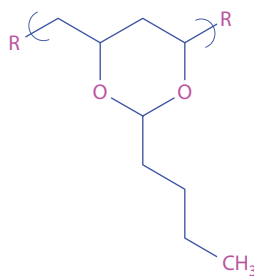
Poly(propylene glycol) (PPG)



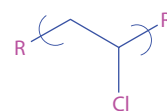
Polystyrene



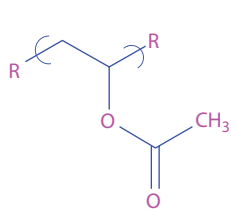
Polytetrafluoroethylene (PTFE)



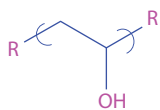
Poly(vinyl butyral)



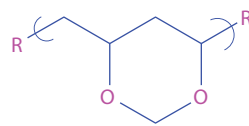
Poly(vinyl chloride) (PVC)



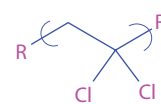
Poly(vinyl acetate)
(PVAc)



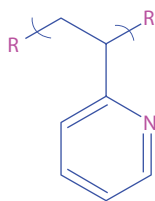
Poly(vinyl alcohol)
(PVA)



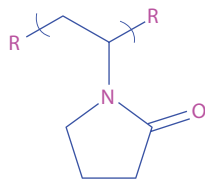
Poly(vinyl formal)
(PVF)



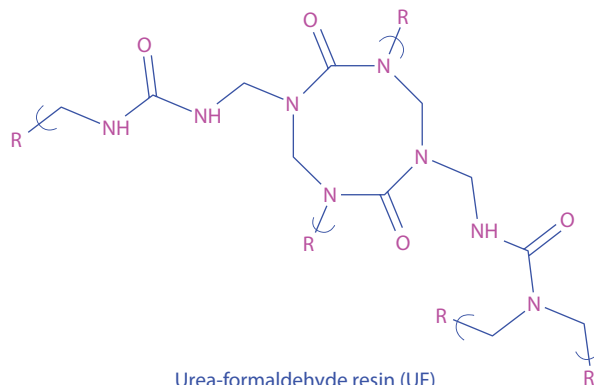
Poly(vinylidene
chloride)



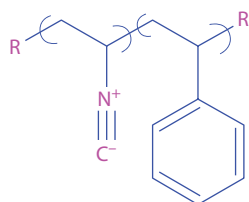
Poly(vinyl pyridine)



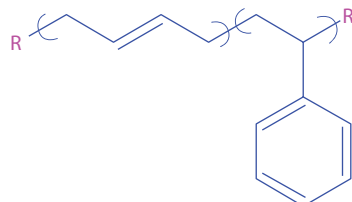
Poly(vinyl pyrrolidone)



Urea-formaldehyde resin (UF)



Styrene-acrylonitrile (SAN)



Styrene-butadiene rubber (SBR)

Appendix B: Symbols and Acronyms

A	Arrhenius constant
ABA	Acrylonitrile-butadiene acrylate
ABS	Copolymer of acrylonitrile, butadiene, and styrene
ACS	Acrylonitrile-chlorinated polyethylene styrene terpolymer
AIBN	2,2'-azobisisobutyronitrile
AMA	Acrylate maleic anhydride terpolymer
AMMA	Acrylate-methyl methacrylate copolymer
AN	Acrylonitrile
ANSI	American National Standards Institute
AP	Ethylene-propylene copolymers
APO	Amorphous polyolefin
AS	Acrylonitrile styrene copolymer
ASA	Acrylonitrile-styrene-acrylonitrile block
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance spectroscopy
AU	Polyurethane
BMC	Bulk molding compound
BPO	Benzoyl peroxide
BSI	British Standards Institution
bp	Boiling point
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAR	Carbon fiber
CED	Cohesive energy density
CFRP	Carbon reinforced plastics
CMC	Carboxymethylcellulose
CN	Cellulose nitrate
COC	Cyclo-olefin copolymer
CPE	Chlorinated polyethylene
CPVC	Chlorinated poly(vinyl chloride)
CR	Neoprene
CTA	Cellulose triacetate
CTFE	Chlorotrifluoroethylene
C_p	Specific heat
C_s	Chain transfer constant
DAIP	Diallyl isophthalate plasticizer
DAP	Diallyl phthalate plasticizer
DNA	Deoxyribonucleic acid
DP	Degree of polymerization
DRS	Dynamic reflectance spectroscopy
DS	Degree of substitution
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_a	Activation energy or energy of activation
E	Young's modulus
EAA	Ethylene acrylic acid copolymer
EC	Ethyl cellulose
ECTFE	Ethylene-chlorotrifluoroethylene copolymer

EEA	Ethylene-ethyl acetate copolymer
EGG	Einstein–Guth–Gold equation
EMAC	Ethylene-methyl acrylate copolymer
EP	Epoxy resin
EPDM	Poly(ethylene-co-propylene) cross-linked
EPM	Poly(ethylene-co-propylene)
EPM	Ethylene-propylene copolymer
EPR	Ethylene propylene rubber
EPR	Electron paramagnetic resonance spectroscopy
EPS	Expanded polystyrene
ESR	Electron spin resonance spectroscopy
ET	Thiokol
ETA	Electrothermal analysis
ETFE	Ethylene tetrafluoroethylene polymer
EU	Polyether polyurethane
EVA	Ethylene-vinyl acetate copolymer
EVOH	Ethylene-vinyl alcohol copolymer
f	Aspect ratio
FEP	Fluorinated ethylene propylene
FRP	Fibrous glass reinforced polyester; fiber reinforced plastic
G	Gibbs free energy; modulus; molar attraction constant
GF	Glass reinforced
GPC	Gel permeation chromatography
GRS	Poly(butadiene-co-styrene)
HDPE	High-density polyethylene
HIPS	High-impact polystyrene
HMC	High-strength molding compound
I	Ionomer
IIR	Butyl rubber
IPN	Interpenetrating polymer network
IR	Infrared
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
K	Constant in Mark–Houwink equation; Kelvin
LC	Liquid crystal
LCP	Liquid crystal polymer
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
LPE	Linear polyethylene
MABS	Methyl methacrylate ABS copolymer
MBS	Methyl methacrylate butadiene styrene terpolymer
MDPE	Medium density polyethylene
MDI	Methylene diphenylisocyanate
MF	Melamine-formaldehyde resin
MP	Melamine phenolic
MWD	Molecular weight distribution
M_n	Number-average molecular weight
M_v	Viscosity-average molecular weight
M_w	Weight-average molecular weight
M_z	Z-average molecular weight
NBR	Poly(butadiene-co-acrylonitrile); nitrile butadiene rubber
NBS	National Bureau of Standards
NMR	Nuclear magnetic resonance spectroscopy
NR	Natural rubber
OI	Oxygen index
P	Phenolic

PA	Polyamide; nylon
PAA	Poly(acrylic acid)
PAEK	Polyaryletherketone
PAK	Polyester alkyd
PAI	Polyamide-imide
PAL	Polyaniline
PAN	Polyacrylonitrile
PARA	Polyaryl amide
PAS	Polyarylsulfone
PB	Polybutylene
PBAN	Polybutylene-acrylonitrile copolymer
PBI	Polybenzimidazole
PBS	Polybutadiene-styrene copolymer
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PCB	Polychlorinated biphenyl
PCL	Polycaprolactone
PCT	Poly(cyclohexylene terephthalate)
PCTFE	Polymonochlorotrifluoroethylene, Polytrifluoromonochloroethylene
PE	Polyethylene
PEEK	Poly(ether ether ketone)
PEG	Poly(ethylene glycol)
PEI	Polyetherimide
PEK	Polyetherketone
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
PET	Poly(ethylene terephthalate)
PEX	Cross-linked polyethylene
PF	Phenol-formaldehyde resin
PGC	Pyrolysis gas chromatography
PI	Polyimide
PIB	Polyisobutylene
PMMA	Poly(methyl methacrylate)
PMP	Polymethylpentene
PMR	Proton magnetic resonance spectroscopy
PMS	Polymethylstyrene
PNF	Poly(phosphonitrilic fluorides)
PO	Polyolefin
PolyEd	Polymer Education Committee
POM	Polyoxymethylene, polyformaldehyde, acetals
PP	Polypropylene
PPC	Chlorinated polypropylene
PPE	Poly(phenylene ether)
POM	Polyoxymethylene
PPO	Poly(phenylene oxide)
PPOX	Polypropylene oxide
PPS	Poly(phenylene sulfide)
PPSU	Poly(phenylene sulfone)
PPT	Poly(propylene terephthalate)
PS	Polystyrene
PTFE	Polytetrafluoroethylene, Teflon
PTME	Poly(tetramethylene terephthalate)
PU	Polyurethane
PUR	Polyurethane rubber
PVA	Poly(vinyl alcohol); sometimes poly(vinyl acetate)
PVAc	Poly(vinyl acetate)

PVAI	Poly(vinyl alcohol)
PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
PVDF	Poly(vinylidene fluoride)
PVF	Poly(vinyl fluoride)
PVK	Poly(vinyl carbazole)
PVOH	Poly(vinyl alcohol)
PVP	Poly(vinyl pyrrolidone)
RIM	Reaction injection molding
RNA	Ribonucleic acid
ROMP	Ring opening metathesis polymerization
ROP	Ring opening polymerization
S	Entropy; radius of gyration
SAN	Poly(styrene-co-acrylonitrile)
SB	Styrene butadiene copolymer
SBR	Poly(butadiene-co-styrene) elastomer
SBS	Styrene butadiene styrene block copolymer
SEBS	Styrene ethylene butylene styrene block copolymer
SEM	Scanning electron microscopy
SI	Silicon
SIS	Styrene isoprene styrene block copolymer
SMA	Poly(styrene-co-maleic anhydride)
SMC	Sheet molding compound
SMMA	Styrene methyl methacrylate copolymer
SN	Sulfur nitride
SPE	Society of Plastics Engineering
SPI	Society of the Plastics Industry
SR	Synthetic rubber
SRP	Styrene-rubber plastics
TDI	Toluenediisocyanate
TEO	Thermoplastic elastic olefin
TGA, TG	Thermal gravimetric analysis
TMC	Thick molding compound
TMMV	Threshold molecular weight value
TPE	Thermoplastic elastomer
TPE	Rubber toughened nylons
TPU	Thermoplastic urethane
TPX	Poly-4-methylpentene
T_c	Ceiling temperature; cloud point temperature
T_g	Glass transition temperature
T_m	Melting point
UF	Urea-formaldehyde resin
UHMWPE	Ultra-high molecular-weight polyethylene
ULDPE	Ultralow-density polyethylene
ULPE	Ultra linear polyethylene
UV	Ultraviolet
VA	Vinyl acetate
VLDPE	Very-low-density polyethylene
WLF	Williams–Landel–Ferry–equation
WS	Polyurethane
XLPE	Cross-linked polyethylene
XPS	Expandable polystyrene

Appendix C: Comments on Health

Most polymers are nontoxic under the normal and intended use. (Some biopolymers, such as snake venom, should not be dealt with except under very controlled conditions.) Most of the additives employed are also relatively nontoxic. Even so, care should be exercised in dealing with many of the monomers of synthetic polymers and when dealing with polymeric materials under extreme conditions such as in commercial and domestic fires.

C.1 FIRE

Fire hazards involve not only burning (most deaths occur from the ingestion of volatiles produced by the fire). Carbon monoxide, the major cause of death, causes unconsciousness in less than 3 minutes due to its preferential attack on hemoglobin.

Interestingly, one important observation concerning burning in general is where colored smoke is produced. Some materials burn producing lots of darkly colored smoke. Some of this colored smoke may be due to the production of aromatic systems including fused ring systems that may contain harmful chemicals including respiratory toxins and cancer-causing agents.

C.2 MEASURES OF TOXICITY

Toxicity involves the effect of various materials on living objects including bacteria, plants, mice, fish, and humans. Tests to determine the toxicity of materials are typically done in a number of ways including inhalation, simple skin contact, and injection under the skin.

While mainly concerned with the effects of various agents on humans, most standard tests are carried out on animals, often a suitable test animal that is believed to be a good model for transferring results from the animal tests to humans. Table C.1 contains some of the toxicity values found in today's literature.

While commercially available, synthetic polymers are relatively nontoxic; the monomers vary greatly in toxicity. This points out the need for monomers and other potentially toxic chemicals to be removed from the polymers. Table C.2 contains the time-weighted average (TWA) for some monomers as cited by the United States Occupational Standards. For comparison, entries for some well-known toxic materials have been added.

C.3 CUMULATIVE EFFECTS

While exposure of the general public to toxins is to be avoided, exposure to people that deal with commercial chemicals on a daily basis is even more important. Such people must take special care to avoid exposure since the toxicities of many of these chemicals are accumulated in our bodies slowly building to levels that may be unhealthy.

Most of the toxic environmentally unwanted chemicals a decade ago have been eliminated from the common workplace. This includes halogenated hydrocarbons such as carbon tetrachloride and aromatic hydrocarbons such as benzene and toluene. Further, chemicals that are known to be potentially toxic, such as some monomers, are being eliminated from the polymeric materials to within the limits of detection.

Industrial recognition of customer and employee safety is a major factor and is included in such international programs as ISO 9000 and ISO 14000. Further, a number of national and state agencies and associations deal with aspects of the environmental and personal safety issues on an ongoing basis.

TABLE C.1 Description of Toxic Measures

TDLo/toxic dose low—The lowest dose introduced by any route other than inhalation over any period of time that causes any toxic effect in humans or produces carcinogenic, teratogenic, mutagenic, or neoplastic effects in humans and animals

TCLo/toxic concentration low—Any concentration in air that causes any toxic effect in humans or produces a carcinogenic, teratogenic, mutagenic, or neoplastigenic toxic effect in humans or animals

LDLo/lethal dose low—The lowest dose introduced by any route other than by inhalation over a time to have caused death in humans or the lowest single dose to have caused death in animals

LD₅₀/lethal dose fifty—A calculated dose expected to cause the death of 50% of a tested population from exposure by any route other than inhalation

LCLo/lethal concentration low—The lowest concentration in air to have caused death in a human or animal when exposed for 24 hours or less

LC₅₀/lethal concentration fifty—A calculated concentration of a substance in air that would cause death in 50% of a test population from exposure for 24 hours or less

EEGL/emergency exposure guideline level—Exposure limits for very short exposure

WEEL/workplace environmental exposure level—Exposure limits for healthy workers exposed repeatedly without adverse health effects

OEL/occupational exposure limits—Worker exposure guide

PREL/permissible exposure limits—Worker exposure limits for no ill effect

NOAEL/no observable adverse effect level—Safe usage level

LOAEL/lowest observable adverse effect level—Safe usage level

TABLE C.2 Time-Weighted Average Values for Selected Monomers and Additional Recognized Toxins

Chemical	TWA (ppm)	Chemical	TWA (ppm)
Acetic anhydride	5	Ethylene oxide	50
Acrylonitrile	20	Formaldehyde	3
Benzene	10	Hydrazine	1
1,3-Butadiene	1000	Hydrogen cyanide	10
Carbon monoxide	50	Phenol	5
Chloroprene	25	Styrene	100
1,2-Ethylenediamine	10	Vinyl chloride	500

C.4 ENVIRONMENT

Today, industry and business recognize that part of doing business is taking care of the environment. Along with various agencies, business and industry are finding that good environmental practices are good business. Advances continue with respect to lowering potentially harmful emissions into our water and air shared by all of us. Chemical industries are taking the lead in this cleanup process. A combination of watchful vigilance and trust is needed to continue this effort.

Appendix D: ISO 9000 and 14000

The International Organization for Standardization (ISO) is an international organization with members in about 100 countries working to develop common global standards.

The **ISO 9000** series encompasses the product development sequence from strategic planning to customer service. Currently, it is a series of five quality system standards with two of the standards focusing on guidance and three contractual standards.

ISO 9000 certification is often obtained to promote a company's perceived quality level, for supplier control, and to promote certain management practices, often total quality management practices. It is acting as a global standardizing "tool" with respect to business and industry in its broadest sense including banking, volunteer organizations, and most aspects of the chemical (including the polymer) industry.

ISO 9000 requires what is called a "third party" assessment but involves developing "first" and "second" party strategies. "First party" refers to the supplier company that requests ISO 9000 certification. "Second party" refers to the customer whose "needs" have been met by the "first party" through the use of quality management procedures achieved through ISO 9000 compliance. "Third party" refers to an outside reviewer that "certifies" that the "first party" has satisfied ISO 9000 procedures.

While **ISO 9000** is a management tool, it affects the way "industry does business" and deals with quality control issues such as how machinery and parts manufactured by a company are monitored for quality. It focuses on satisfying the "customer," the "purchaser" of the raw materials, manufactured parts, or assembled items and includes the eventual "end customer"—the general public. It is an attempt to assure quality goods.

ISO 14000 is a series of standards intended to assist in managing the impact of manufactured materials including finished products and original "feedstocks." It addresses the need to have one internationally accepted environmental management system that involves "cradle to grave" responsibility for manufactured materials emphasizing the impact of products, operations, and services on the environment.



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Appendix E: Web Information

The information concerning polymers on the World Wide Web is rapidly expanding. This is a valuable source of information giving both applied and fundamental information on a wide range of polymer-related topics. As you search, please be aware that there exist specific pooled information sites on many topics including those considered “hot” topics such as the human genome. There are also web clusters that deal with special topics such as nanomaterials and electrically conductive materials. Have fun “surfing the web.” It is an important source of information about polymers. Wikipedia is also a great place to start for general information about polymers and polymeric materials. But please remember it is not rigidly referred so it is not a primary source of information for publishing, using in theses, research papers, and books.

Sites that you should consider visiting and that are not obvious because of their names are as follows:

www.polyed.org, which is a general site for [PolyEd](#), the joint polymer education committee of the American Chemical Society Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering. It contains many connections to other important websites dealing with polymers.

The Polymer Ambassadors have their own site at www.polymerambassadors.org.

www.pslc.ws/macrog/index.htm, or simply type in “[macrogalleria](#)” and you will be taken to a fun and educational website that focuses on the relationship between everyday items and their polymeric nature and the fundamentals that underlie their use in these materials.



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